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Final Report

July 1966 - July 1969

Investigation of Polymer Encapsulation of Cotton Fibers

To Provide New and Useful Textile Products

Prepared by

New York University

for

U S D A

Southern Utilization Research and Dev. Division

under

Contract # 12-14-100-8911-(72)

with the

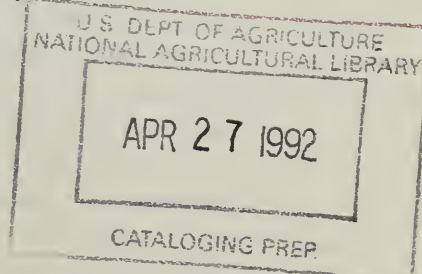
U S D A

Southern Utilization Research and Dev. Division

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Prepared by Walter Brenner

Barry Rugg



UNITED STATES DEPARTMENT OF
AGRICULTURE
AGRICULTURAL RESEARCH SERVICE

REPORT TO
SOUTHERN REGIONAL RESEARCH CENTER
NEW ORLEANS, LOUISIANA

CONTRACT PROJECT REPORT
(To be used as cover sheet for report)

Contracting Organization
New York University

Project Leader
Walter Brenner

Department Division of Applied Science
(Originally performed by School of Engr'g)

USDA Designated Representative
Stanley P. Rowland

Section

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Investigation of Polymer Encapsulation of Cotton Fibers to
Provide New and Useful Textile Products

ABSTRACT OF PROGRESS

There is a recognized need for the development of more effective chemical treatments. in order to impart to cotton fabrics improved service characteristics particularly as relates the attainment of durable press performance with minimal strength losses and retention of abrasion resistance. Polymer encapsulation of cotton fibers and fabrics was experimentally investigated as a novel approach for developing cotton textiles with an optimum balance of use characteristics. Experiments were carried out on the vapor phase in situ polymerization of selected vinyl monomers such as ethyl acrylate, glycidyl methacrylate, ethylcyanoacrylates, etc., in order to deposit continuous polymer films on cotton fiber substrates. Nylon 610 polymer coatings were obtained by interfacial polymerization techniques. Polyformaldehyde polymers were also deposited on alkali treated cotton substrates via an in situ vapor phase polymerization process. Polymer deposits ranging from as little as 2% to over 50% by weight of the cellulosic substrates could be reproducibly obtained by appropriate changes of processing parameters. Subsequent polymer and cellulose cross linking was carried out where applicable and the performance properties of the polymer treated cottons determined by standard test methods. Additionally, photomicrographs were taken in order to characterize the location of the polymer deposits and the structure of the polymer/cotton composites. Certain cross linked polyformaldehyde treated cottons showed a superior balance of performance properties.



I. Introduction

During the past decade there has developed not only a steadily increasing appreciation of the very great economic and technical importance of the cotton textile industries but also recognition of the tremendous potential not only for retention of present cotton markets but also development of new volume applications which can be realized by effecting a wide range of improvements in properties that can be added to cotton through chemical research.¹⁾²⁾³⁾ While cotton is a most versatile fiber and is particularly attractive where comfort is a primary consideration, it is deficient by comparison to synthetic fibers in several specific performance properties such as abrasion resistance, toughness, thermoplasticity, water repellency, drying rate and luster. Also some of these deficiencies are the more pronounced for the cross-linked cottons. It is desirable, therefore, to impart such necessary improvements to cotton at a low cost. The extent to which this is being carried out in industry, is well indicated by recent market data which predict a rise in the annual market of chemicals used for such treatments from a present 75-80 million # to as much as 105-115 million # within the next two years.⁴⁾

Undoubtedly great strides have been made in imparting to cotton by diverse suitable chemical treatments such valuable service characteristics as wash and wear properties, durable crease, stretch etc. It has proven most difficult however to develop an optimum balance of fiber properties with conventional economically competitive treating technology. Thus, for example, many studies have shown that when cotton fabrics are subjected to chemical treatments for the improvement of abrasion resistance and breaking



strength, tear strength and crease recoveries are significantly degraded.⁵⁾⁶⁾ Similar problems develop with other pertinent fiber properties. The limitations of the presently practiced chemical treating technology in achieving an optimum balance of cotton fiber properties have generated interest in evaluation of the technical and economic potential of other less conventional processing techniques.

The encapsulation of cotton fibers, yarns or fabric within ultra-thin sheaths of selected polymers offers an attractive route for the improvement in the abrasion resistance and certain other cotton fabric properties with minimum alteration of their desirable features. Specifically this technique - especially when applied from the vapor phase - offers an interesting potential means for overcoming the disadvantages of wet finishing operations by providing individual fibers within a yarn or fabric with microscopical sheaths of polymer without deleteriously affecting existing advantageous characteristics of the fabric and the basic physico/chemical structure of the cotton fibers. Furthermore, recent studies have emphasized a close relationship between surface properties and friction and recent exploratory data have experimentally demonstrated that polymer encapsulation of cotton fibers can be realized with little or no degradation in physical strength properties. The ability to provide individual fibers with microscopic shells of preselected polymers of controllable thickness and molecular weight without, as noted above, affecting the more desirable properties and basic structure of cotton fibers not only overcomes certain disadvantageous features of the presently practiced technology but appears to offer various additional advantageous features especially for maximizing the abrasion resistance etc. of cotton.

The general objectives of this study have been to plan and conduct exploratory investigations of polymerizations on the surface of cotton fibers, designed to explore monomers, catalysts, processes and conditions necessary for deposition of thin films of polymer for encapsulation of the cellulosic fibers and to characterize and evaluate the quality of the encapsulation to obtain data to serve as a basis for improving specific performance properties of cotton fabrics. More specifically, the suitability of vapor phase processes in relation to liquid phase polymerizations has been evaluated for the deposition of polyethylacrylate and other suitable polymer films, particularly to establish the relative advantages of the polymerization from the vapor phase on cotton fibers and to properly characterize and establish the nature of such polymer films and the degree of control of quality thereof. Also investigations have been conducted to determine the type and design of equipment and techniques suitable for laboratory scale encapsulation of cotton fibers, and cotton fibers in yarns and in fabric, in quantities sufficient for conventional polymer characterization and fiber, yarn and fabric evaluations.

Studies have been carried out to characterize the deposition of various polymer films on cellulose substrates in terms of meaningful performance parameters. Specifically, the polymers studied were polyethylacrylate, polyglycidyl methacrylate, polymethyl cyanoacrylate, polyoxymethylene (polyformaldehyde), and nylon 610. These polymers were applied via numerous different techniques including vapor phase in situ polymerization and interfacial polymerization (both liquid-vapor and liquid-liquid). Subsequent polymer and cellulose cross linking was carried out where applicable and performance properties were measured and analyzed. Additionally, physical

characterization of polymer encapsulated cotton substrates was accomplished by the development of photomicrographic analysis of certain of the more interesting sample products. The following will include an in-depth discussion of all aspects of the three year experimental program herein briefly described.

II. Experimental, Results and Discussion

A. Vinyl Monomers - Addition Polymerization

All experimental work was conducted with desized, scoured, bleached 80 x 80 print cloth supplied by the U.S. Dept. of Agriculture, Southern Utilization Research and Development Division, from which 6" x 6" samples were cut for use in the subsequently described vapor phase polymerization studies. All samples were first dried in a circulating air oven and uniformly conditioned at ambient temperature before weighing. For the vinyl monomer vapor phase polymerizations the samples were then immersed for predetermined time periods in a catalyst solution at a controlled temperature. The activated cloth samples were dried under controlled conditions for 10 minutes at ambient temperatures and hung in stainless steel frames which were suspended inside a 8" x 8" x 12" stainless steel lined vacuum oven. Monomer was then admitted mixed with nitrogen carrier gas and another catalyst component if required. Times of exposure of the thusly treated cotton cloth samples were varied at predetermined temperatures. The samples were washed and dried etc. prior to final weight measurements. All weight gains reported are after appropriate water treatments or solvent extractions for determination of % grafted vs. homopolymer. A sketch and flow sheet of the equipment set up and procedures is shown in Figures #1 and #2. Note that the vacuum oven served as the vapor phase polymerization reactor.



FIG. 1: APPARATUS FOR VAPOR
PHASE COATING OF COTTON
CLOTH WITH POLYETHYLENE
ACRYLATE, etc.

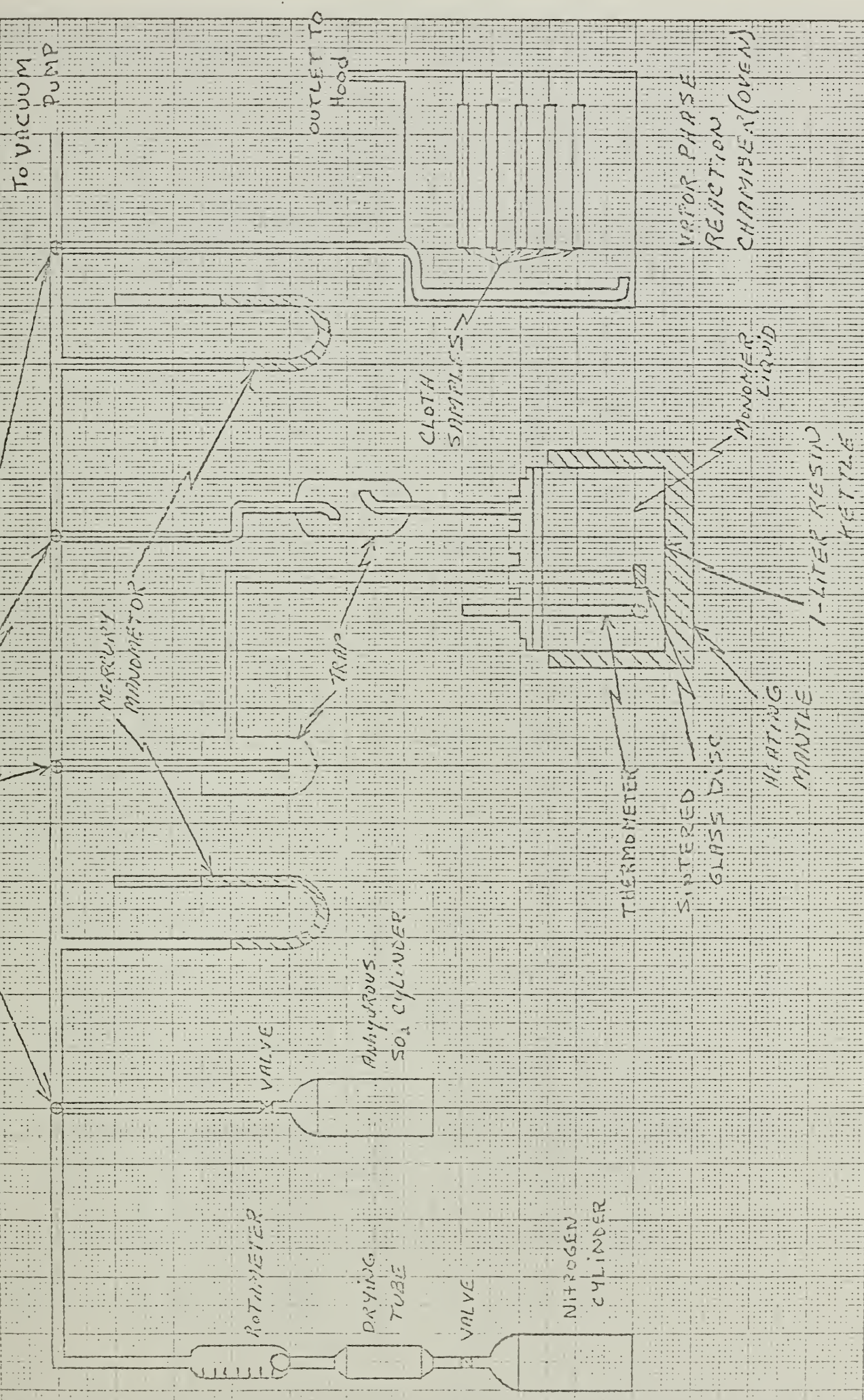
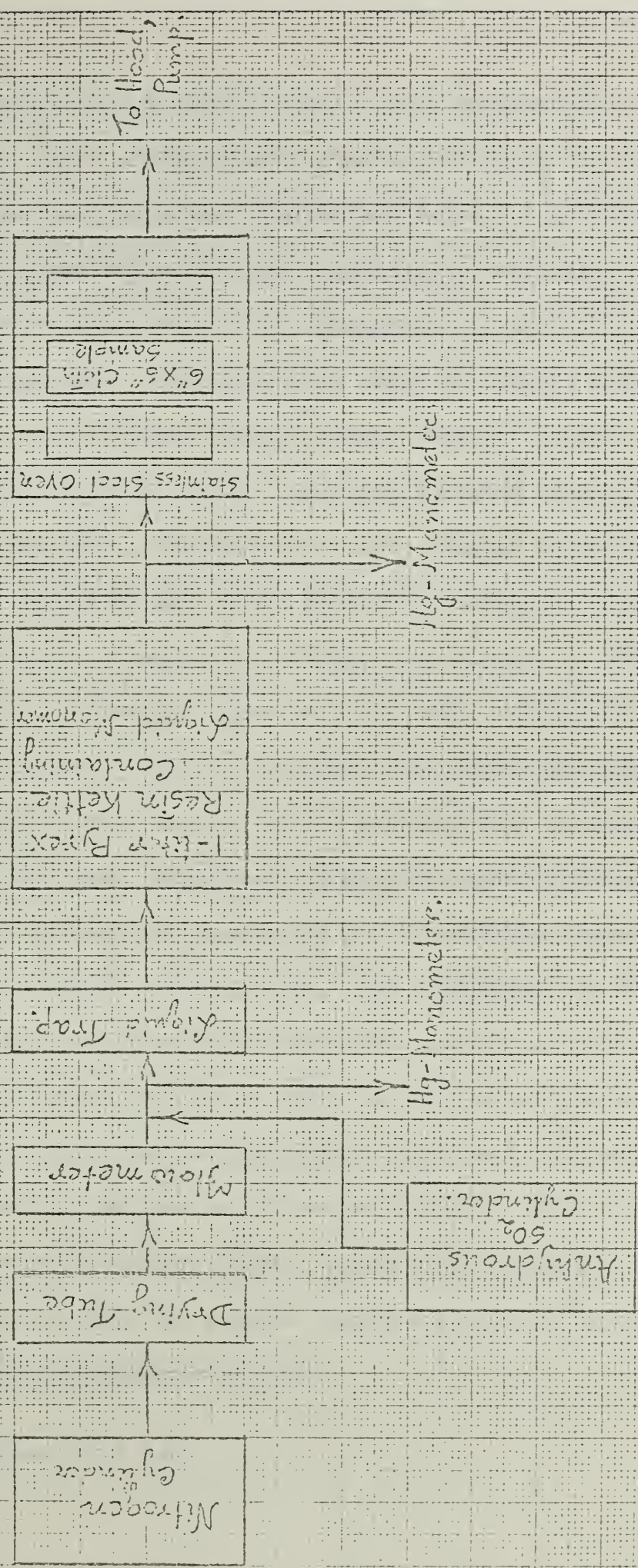




Fig. 2: Flow Sheet Of The Vapor Phase Encapsulation Process.



A number of vinyl type monomers were employed for these exploratory vapor phase polymerization studies including alkyl acrylates, cyanoacrylates, acrylonitrile and methacrylonitrile. A considerable amount of experimentation was conducted with cyanoacrylate and alkyl acrylate monomers as "model" compounds for the development of appropriate vapor phase polymerization reactions. Cyanoacrylates could be readily polymerized from the vapor phase onto cotton fibers without added external catalyst, the small amounts of residual moisture of the conditioned cotton fiber cloth samples serving in that capacity. Methylcyanoacrylate polymer coatings of up to 30% by weight of the weight of the cotton fibers were obtained after exposure of cloth samples to monomer vapor in a nitrogen gas carrier at 95°C for less than 90 minutes^{*}; a 22% weight gain was found after approximately 1 hour's exposure to 95°C monomer vapor. The sample cloth swatches were maintained at ambient temperatures while exposed to the cyanoacrylate monomer and the nitrogen carrier mixture gas flow. Experiments including appropriate microscopic studies have been carried out and are continuing on the suitable characterization of the thusly polymer coated cotton fibers. The dissolution of the cotton cellulose in 1M cupriethylenediamine hydroxide solvent at ambient temperatures leaves well formed continuous hollow methylcyanoacrylate polymer shells. Consideration is being given to experiments which would attempt to relate the weight of residual polymer to the add-on obtained after vapor phase polymerization onto the cotton fibers. Based upon admittedly incomplete extraction studies in DMF, the polymer deposits appear to be overwhelmingly homopolymer methylcyanoacrylate (> 95%).

* Monomer contained 0.1% P₂O₅

1. Ethyl Acrylate

The ethyl acrylate monomer was polymerized onto the surfaces of the cotton fiber by means of an ammoniumpersulfate-sulfur dioxide redox catalyst system. The conditioned cotton cloth samples were immersed in a 2 weight % aqueous ammonium persulfate solution for time periods ranging from 1 second to 5 minutes. They were then exposed to ethyl acrylate monomer vapors containing anhydrous sulfur dioxide (redox couple) and nitrogen carrier gas while at ambient temperature in the reactor. Typical data for ethyl acrylate monomer are shown in Table #1. The polymer coated cotton cloth was treated as described previously to ascertain weight gain and % graft polymer content.* Dissolution of the cotton fibers in 1M cupriethylenediamine hydroxide solvent at ambient temperatures resulted in hollow polymer shells which are quite benzene soluble under those vapor phase polymerization conditions resulting in essentially homopolymer formation. Infrared analytical data attached to this report further confirm the formation of ethyl acrylate homopolymer on the cotton fiber surfaces (Figure 3).

These and many similar experiments indicate that longer catalyst immersion periods result in increasing amount of grafting in place of homopolymer formation, all other experimental variables being kept constant. This can be related to the rate of diffusion of the catalyst solution into the interior of the cotton fibers and should also be a function of the initial moisture content of the cotton fibers. Homopolymerization or encapsulation appears to be directly related to the ability of the experimenter to restrict the polymerization reaction to the fiber surfaces only by the establishment of appropriate reaction conditions. The experiments utilizing the so-called

* Soxhlet extraction: 20 hours benzene

Table #1. Vapor phase polymerization of ethyl acrylate monomer vapor onto cotton fibers.

(ammoniumpersulfate-sulfur dioxide redox catalyst; monomer temperature kept constant at 90°C)

Sample designation	Initial cloth sample Wt (A), grams	N ₂ flow rate liters/min.	N ₂ + anhyd.SO ₂ gas flow rate, cm Hg	Cat.Solution Dipping Time, seconds	Monomer Vapor Exposure Time, min.	Wt.of Cloth monomer vapor exposure (B), gms	% weight gain of cloth $\frac{B-A}{B} \times 100$	Wt.of cloth after solvent extraction (C) gms	% graft polymer formed $\frac{C-A}{B-A} \times 100$
2-1-4	2.592	0.195	9.0	1.0	60	2.688	3.7	2.594	0.28
2-1-4'	2.572	0.195	9.0	1.0	60	2.662	3.5	-	-
2-2-4	2.623	0.195	9.0	15.0	60	2.772	3.8	2.625	0.22
2-2-4'	2.534	0.195	9.0	15.0	60	2.635	4.0	-	-
2-3-4	2.654	0.195	9.0	30.0	60	2.759	3.95	-	-
2-3-4'	2.574	0.195	9.0	30.0	60	2.681	4.15	2.577	1.0
2-4-4	2.633	0.195	9.0	60.0	60	2.744	4.2	2.635	0.9
2-4-4'	2.533	0.195	9.0	60.0	60	2.658	4.1	-	-
2-5-4	2.608	0.195	9.0	300.0	60	2.722	4.4	-	-
2-5-4'	2.559	0.195	9.0	300.0	60	2.669	4.3	2.571	9.2

* Data corrected for wt. loss of uncoated cloth samples for same extraction conditions (1.8%)



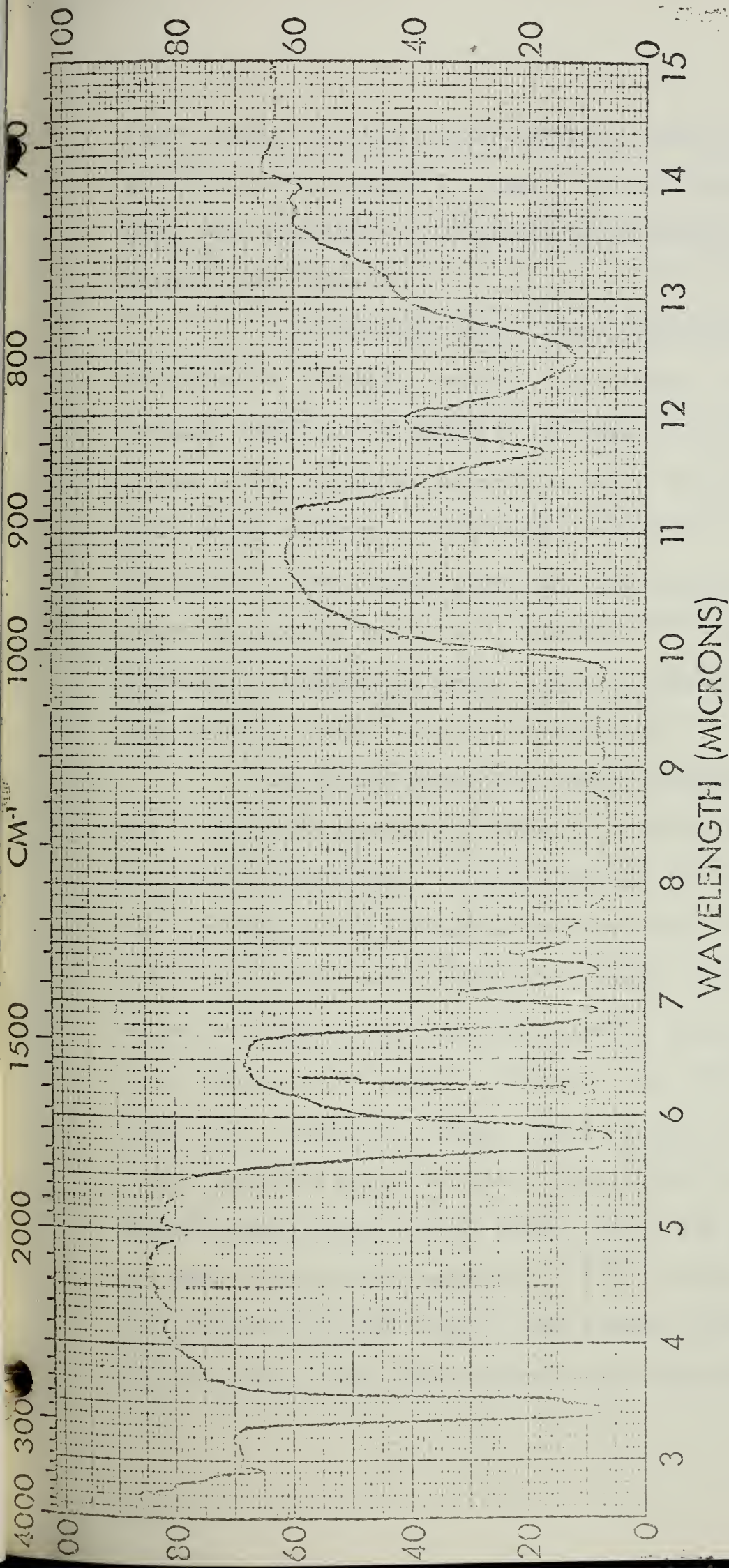


Fig. 3. I.R. Spectrum of Extracted Polyethyl Acrylate.

Film on NaCl Plate from Benzene Solution.



"redox couple" catalyst system comprising sulfur dioxide and ammonium persulfate have resulted in strength losses of the coated cotton fabrics which were considered to be related to the acidity of the sulfur dioxide catalyst (see Table 2).

An alternative vapor phase polymerization system based on the employment of an organic peroxide type catalyst system has been experimentally studied in an effort to overcome the disadvantageous characteristics of the previously referred to sulfur dioxide-potassium persulfate redox couple catalyst. The reaction mechanism of such a peroxide catalysis is typical of free radical initiated vinyl polymerization and has been extensively reported on in the literature.⁽⁷⁻¹⁰⁾ Such polymerizations can be performed in homogeneous media, either in bulk or solution, or in heterogeneous media, either emulsion or suspension.

As is well known free radical polymerizations are exothermic and can be initiated chemically, thermally, photolytically and by radiation with and without sensitizers. Organic peroxides and related catalysts are among the most widely used polymerization initiators because these compounds are soluble in acrylic ester monomers and permit control of the reaction and the molecular weight of the resulting polymeric products by the selection and concentration of the specific initiator used, monomer concentration, temperature, etc. During the initial stages bulk and solution polymerization of acrylic monomers proceed at rates that are first order with respect to monomer concentration and the square root of the initiator concentration and that increase with temperature.⁽¹⁰⁻¹²⁾ Autoacceleration of the rate of bulk polymerization of acrylic ester monomers typically begins at around 20% conversion during which stage the rate and molecular weight increase

rapidly to high conversions.⁽¹³⁾ The rate then drops quickly at limiting conversion which depends on the temperature, viscosity, molecular weight and glass transition temperature.⁽¹⁰⁻¹³⁾ These factors must be duly taken into consideration in the design and execution of monomeric acrylic ester polymerization studies.

Fabric samples of 10" x 6" size were cut from the variously polymer treated cloths for use in the polymer deposition and cross linking experiments as well as the fabric evaluation which have been summarized in Table #2.

The vapor phase polymerization and cotton cloth coating equipment which is schematically represented in Fig. #4, is based on the 8" x 8" x 12" stainless steel oven which was employed as the polymerization chamber for these peroxide catalyzed experiments. This vacuum oven could be used for carrying out both vacuum and pressure experiments by the installation of appropriate gasketing. Previously conditioned and weighed cotton cloth samples sized 10" x 6" were immersed in a methyl ethyl ketone solvent solution containing 3% by wt. of benzoyl peroxide, at ambient temperatures. They were then heated at 30-35°C in air for approximately 30 minutes to evaporate the solvent. These catalyst activated cotton cloth samples were mounted on stainless steel frames which were then suspended inside the preheated polymerization chamber from a suitably positioned stainless steel rack. Typically, the temperature of the polymerization chamber was maintained at 100°C.

A 29" vacuum was then pulled on the heated polymerization chamber and predetermined amounts of monomer introduced from a calibrated storage vessel through a tube at the base of the chamber, the ethyl acrylate monomer flashing rapidly to create an ethyl acrylate vapor atmosphere.



Table 2. Physical properties of polyethyl acrylate coated cotton cloths cross linked with Permafresh 183

Sample	% Ethyl Acrylate Add-on	% Permafresh 183 Add-on	(1) Breaking Strength (lb.) (% Retention)		(2) Elongation	Abrasion (3) Cycles to Failure	(2) Tear Strength (gm)		(4) Wrinkle Recovery (W + F)	
			Warp	Wet			Warp	Dry	Dry	Wet
Control	-	-	53.4 (100)		5.7	107	413	162	155	
C-1	3.8	-	51.2 (95.9)		5.3	110	400	170	168	
C-2	13.4	-	48.0 (89.9)		5.2	112	410	169	165	
C-3	18.8	-	54.0 (101.1)		5.8	106	415	180	166	
C-4	27.5	-	50.0 (93.7)		5.6	109	402	155	160	
C-5	40.4	-	55.6 (104.1)		5.7	120	406	164	162	
CP-1	-	3.0	28.3 (53.0)		4.2	56	331	297	295	
CP-2	-	1.9	29.6 (55.4)		4.3	54	325	283	275	
CP-3	-	1.5	29.8 (55.8)		4.6	55	330	280	285	
CP-4	-	1.0	32.0 (59.9)		4.1	75	384	275	270	
CP-5	-	2.5	31.0 (58.1)		4.0	62	379	290	266	
(1) ASTM D 1682-64 (Average of 5 runs)							(3) ASTM D 1175-64T (Average of 5 runs)			
(2) ASTM D 1424-63 (Average of 5 runs)							(4) ASTM D 1295-60T (Average of 5 runs)			



Table 2. Physical properties of polyethyl acrylate coated cotton cloths
(cont'd)
cross linked with Permafresh 183

Sample	% Ethyl Acrylate Add-on	% Permafresh 183 Add-on	(1) Breaking Strength(lb) (% Retention) Warp	(2) Elongation %	Abrasion (3) Cycles to Failure	Tear Strength(2) (gm) Warp	Wrinkle(4) Recovery (W + F) Dry	Wet
(30)-31-69	3.8	1.8	33.0 (61.8)	3.9	79	288	280	276
32-39-(29)	4.3	2.0	32.8 (61.4)	4.4	68	309	285	283
(35)-38-67	2.9	1.7	29.2 (54.7)	3.9	58	336	283	285
(36)-75-86	2.3	2.4	29.8 (55.8)	4.1	73	272	284	280
(37)-83-68	3.0	1.8	30.7 (57.5)	3.8	70	240	288	278
42-(76)-84	3.6	3.3	30.8 (57.7)	4.1	68	251	282	276
70-82-(85)	4.5	2.0	29.8 (55.8)	4.1	75	283	292	286
(72)-73-75	1.5	2.8	29.5 (55.3)	4.0	65	309	301	285
(40)-43-71	5.4	2.2	38.1 (71.4)	4.3	79	261	293	282
(41)-45-62	6.3	2.0	37.2 (69.6)	4.1	60	299	295	297

(1) ASTM D 1682-64 (Average of 5 runs)
(2) ASTM D 1424-63 (Average of 5 runs)
(3) ASTM D 1175-64T (Average of 5 runs)
(4) ASTM D 1295-60T (Average of 5 runs)

Table 2. Physical properties of polyethyl acrylate coated cotton cloths
(cont'd) cross linked with Permafresh 183

Sample	% Ethyl Acrylate Add-on	% Permafresh 183 Add-on	(1) Permafresh Breaking Strength(lb) (% Retention) Warp	(2) % Elongation	Abrasion (3) Cycles to Failure	Tear Strength (2) (gm) Warp	Wrinkle (4) Recovery (V + F) Dry	Wet
(44)-47-48	6.6	1.5	36.4 (68.2)	4.4	73	267	293	280
(46)-57-63	8.5	2.3	38.4 (72.0)	4.4	65	277	282	268
(52)-49-53	9.5	1.0	36.0 (67.4)	4.3	75	283	280	272
(50)-54-65	11.4	1.4	37.0 (69.2)	4.2	80	283	275	270
(58)-64-66	11.6	1.5	35.5 (66.4)	4.0	110	293	285	282
25-(26)-56	13.3	1.0	37.3 (69.9)	4.8	115	251	283	284
(51)-55-59	13.0	1.2	39.5 (73.9)	4.2	97	261	275	273
27-(28)-60	15.8	1.3	38.2 (71.5)	4.6	88	272	301	285
61-21-(22)	17.5	1.2	37.8 (70.8)	4.6	95	283	293	295

(1) ASTM D 1682-64 (Average of 5 runs)

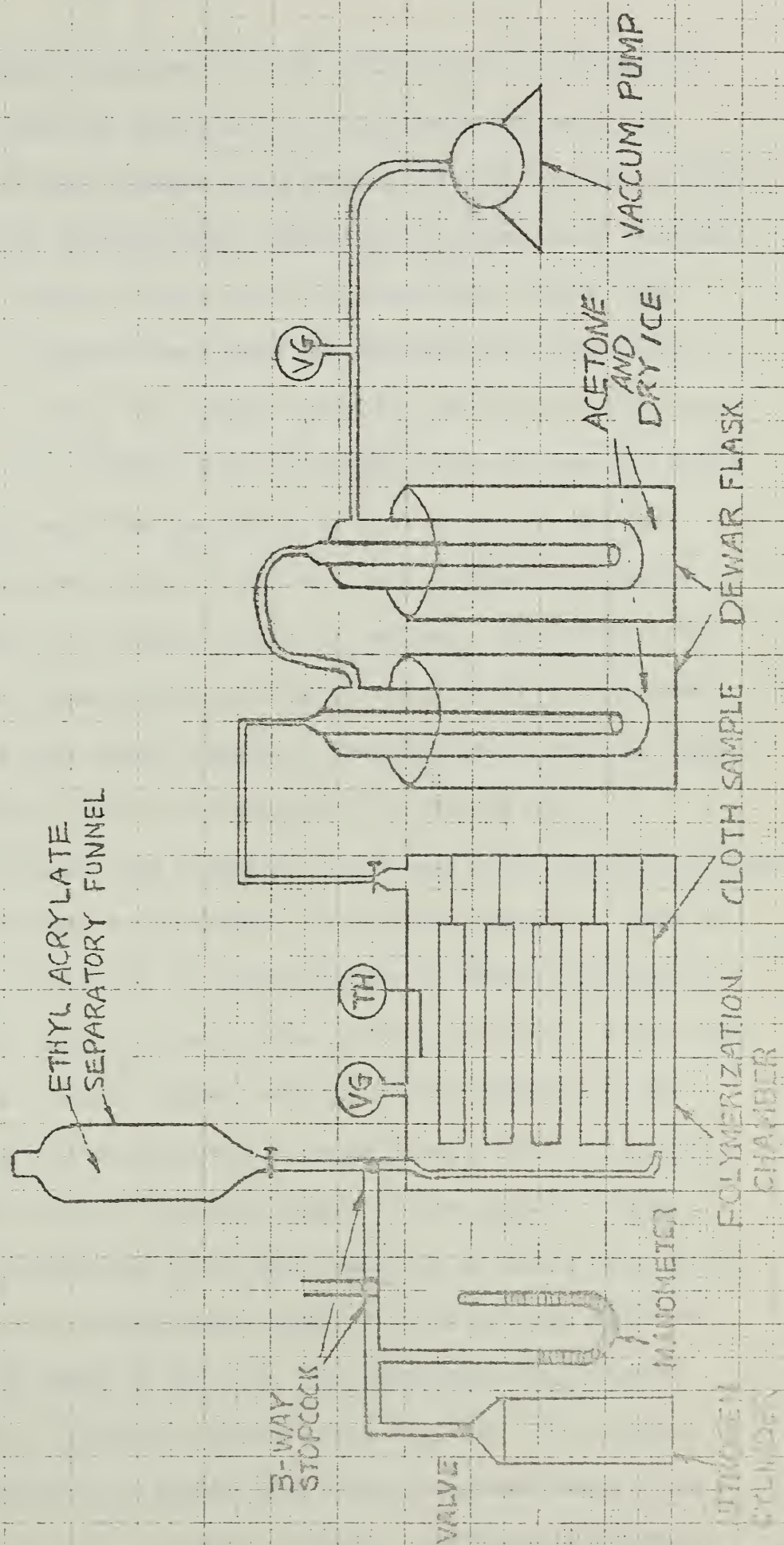
(2) ASTM D 1424-63 (Average of 5 runs)

(3) ASTM D 1175-64T (Average of 5 runs)

(4) ASTM D 1295-60T (Average of 5 runs)



FIGURE 4. SCHEMATIC DIAGRAM OF VAPOR PHASE COATING
OF COTTON CLOTH WITH ETHYL ACRYLATE



The vacuum was then gradually released with the introduction of controlled amounts of nitrogen gas till the equivalent of atmospheric pressure was attained. The addition of the nitrogen gas promoted agitation of the gaseous atmosphere and was found to significantly enhance the uniformity of the polymerization of the ethyl acrylate monomer onto the activated cotton cloth fabric surfaces. After a preset time period the reaction was terminated by again pulling a vacuum to remove the monomer remaining in the polymerization vessel. The vacuum was then released and the samples removed from the polymerization chamber. They were then permitted to cool in air to ambient temperatures, washed to remove unreacted monomer, etc., dried to constant weight, etc. and the amount of polymer add-on determined. Experiments were carried out in which the polymer add-on's were varied from 3% to 40% based upon the weight of the cotton fabric samples. The effects of reaction time and concentration on polymer add-on are shown in Fig. #5 and #6.

Extraction studies were carried out on these ethyl acrylate polymer coated cotton fabrics in order to ascertain the relative amounts of homo and graft polymers formed. The amount of polymer extracted after a 24 hour refluxing period in Soxhlet extractor was in the order of 97-98 wt. % and more based upon the wt. of the initial polymer add-on. Upon treatment of the polyethylacrylate coated cotton fabrics with cuene the cotton cellulose dissolved completely leaving behind tube-like shapes of the acrylic polymer. The polymer deposit was identified by infrared analysis of films made of the material extracted from the cotton fabric samples by the toluene solutions. This infrared spectrum is shown in Fig. #7. For comparison the infrared spectrum of ethyl acrylate polymer is presented in Fig. #8. The polymer melting point was determined in a Fisher John's apparatus and found to be identical with that reported for polyethylacrylate. Differential staining

FIGURE 5. PERCENT ADD-ON VS REACTION TIME
FOR REACTION AT 100°C AND 1.85 GM/L
MONOMER CONCENTRATION

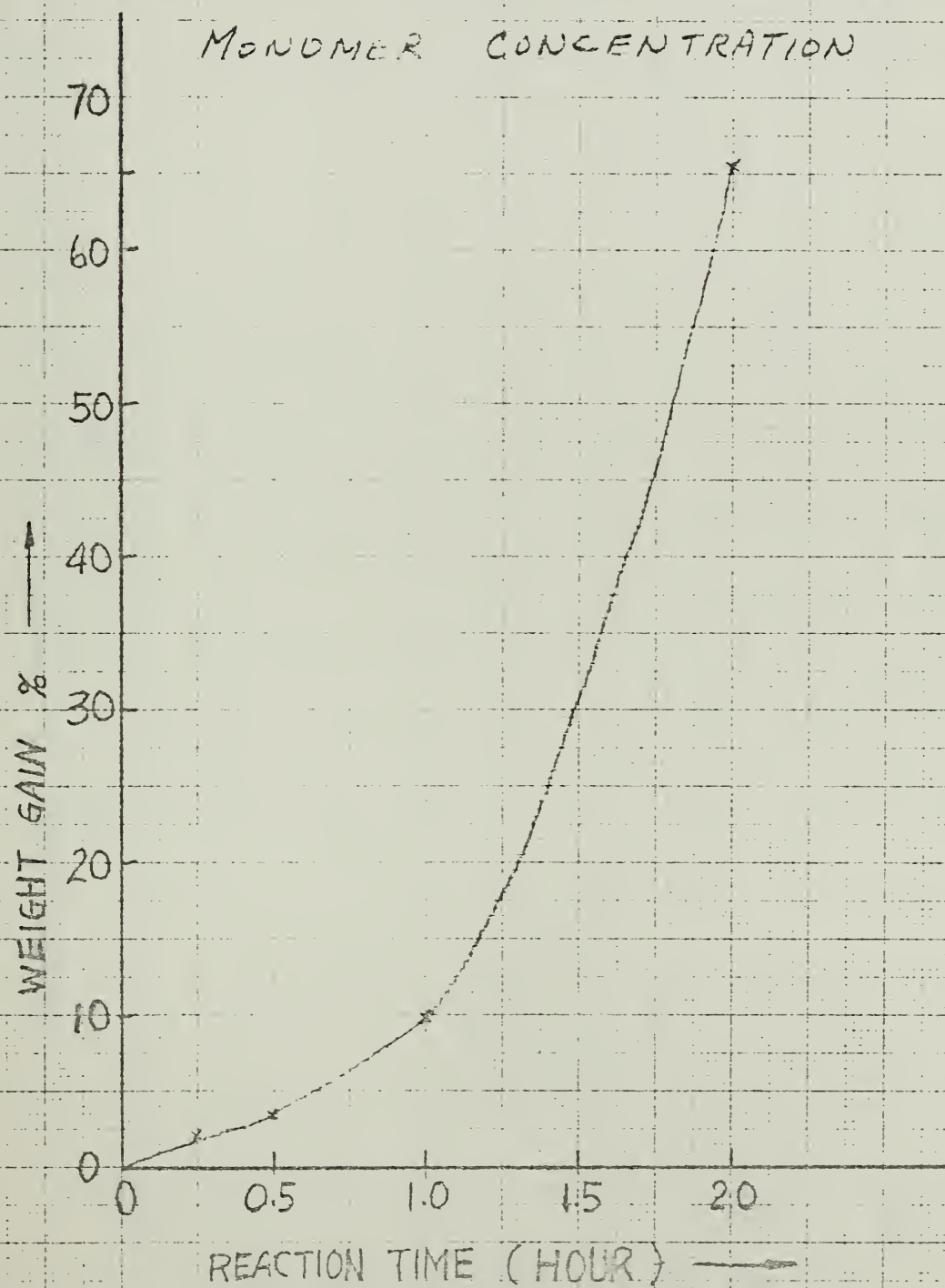
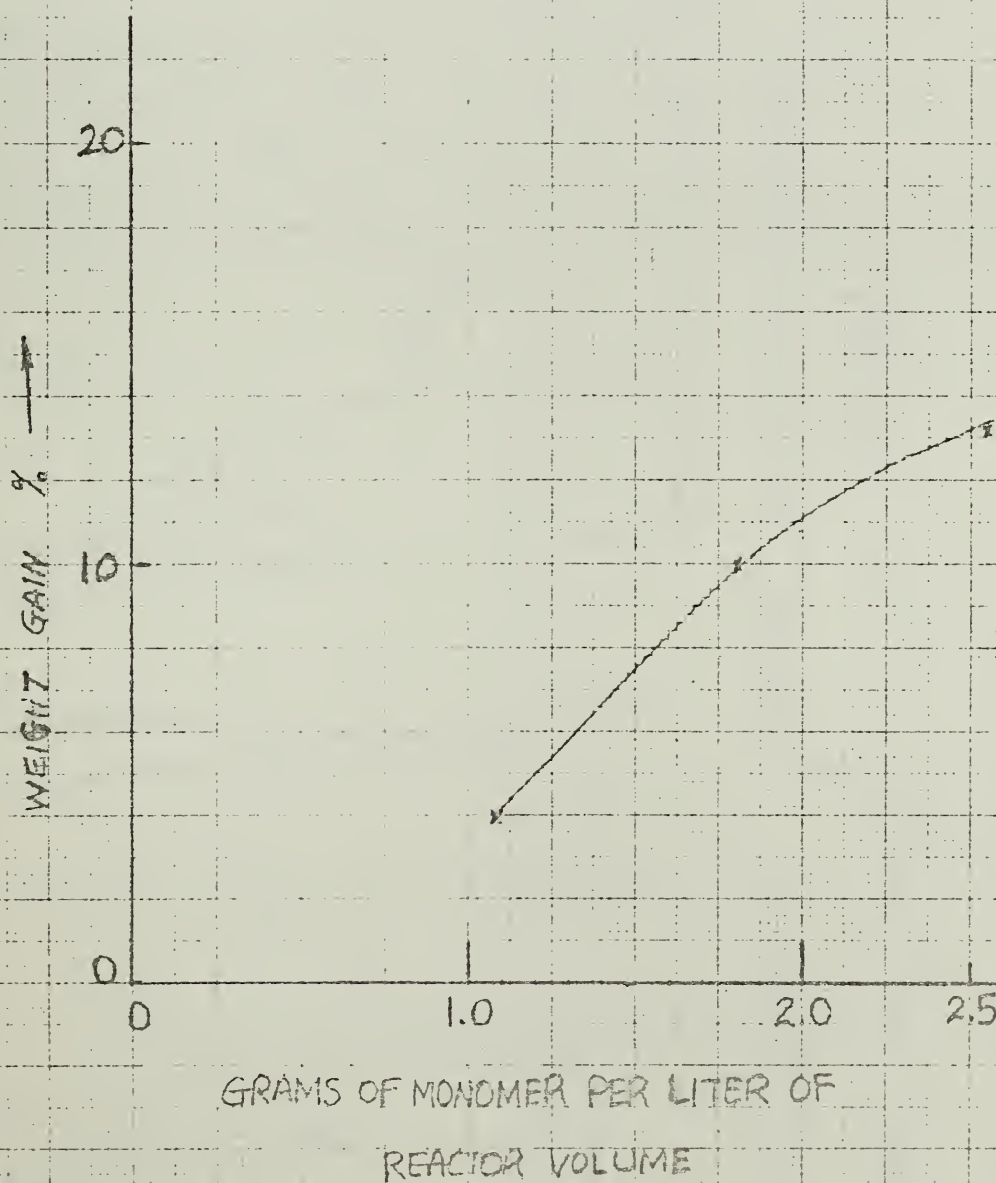
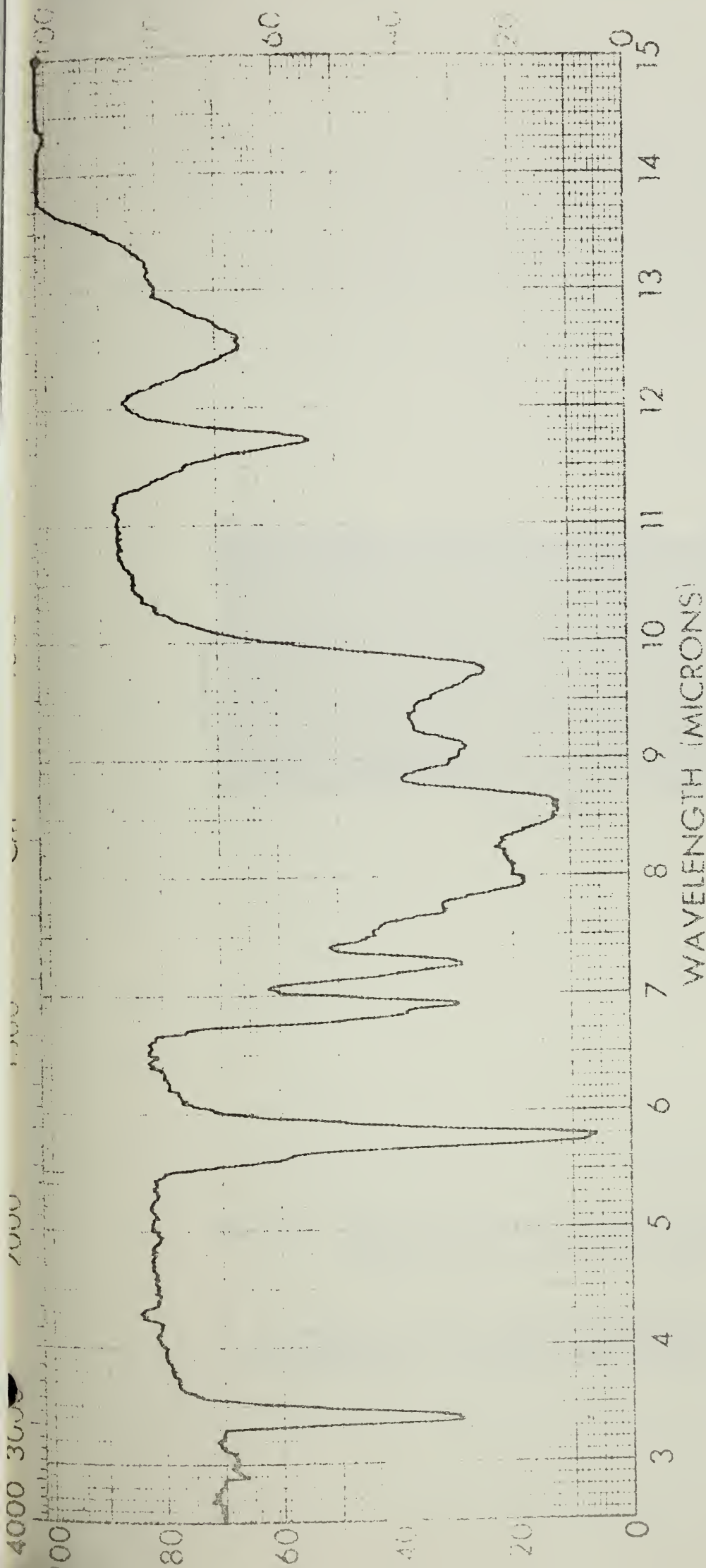


FIGURE 6. PER CENT ADD-ON VS. CONCENTRATION
FOR REACTIONS AT 100°C FOR 1 HOUR







SPECTRUM NO. _____
SAMPLE _____

20.

SPECTRUM NO.	ORIGIN	LEGEND	REMARKS
1. Ethyl Acrylate	Toluene solution	1.	
2. polymer extracted from cotton coated samples	evaporated to NaCl plate	2.	
	PURITY	DATE 12/2/69	
	PHASE	OPERATOR B. Ruzg	
	THICKNESS		

Fig. 7. Polyethyl acrylate film on NaCl plate from toluene solution.



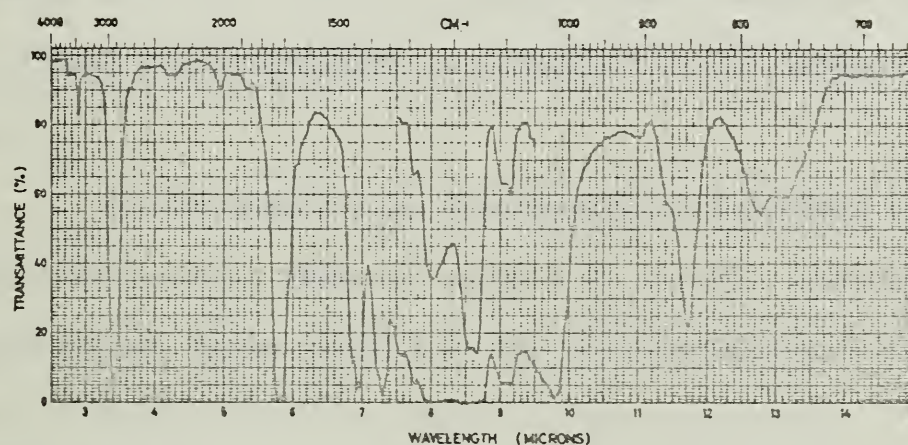


Fig. 8. Polyethyl acrylate film on NaCl plate
from ethylene dichloride solution *

* J. Haslam, et al., Identification and analysis
of plastics, D. Van Nostrand and Co., 1965.

of polymer deposited cotton fiber sections is being carried out in order to ascertain the location and characteristics of the polyethylacrylate deposits.

Fabric performance parameters such as tensile strength properties, tear strength and Monsanto wrinkle recoveries were determined as a function of polymer add-on as is shown in Table #2. Compared to control cotton samples the strength properties including tear strength were unchanged even up to 40 wt. % polymer add-on's and abrasion resistance values were found to be somewhat improved. There was experienced however no significant change in shape holding characteristics as indicated by the Monsanto wrinkle recovery values.

In accordance with considerations described in the previously submitted semi-annual progress reports #4 and #5, experiments were therefore initiated on the cross linking of the polyethylacrylate coated cotton fabrics in order to develop improved shape holding properties. A conventional methylolamide cross linking agent system based on Permafresh 183 resin and Catalyst X-4 was employed for these cross linking studies.

A rather typical simplified cross linking agent treating solution was accordingly prepared which consisted of the following components:

Permafresh 183	96 pts. by wt.
Catalyst X-4	20 pts. by wt.
Mykon SF	40 pts. by wt.
Triton X-405	20 pts. by wt.
Water	2000 pts. by wt.

The polyethylacrylate polymer coated cotton fabric samples were padded with this cross linking agent solution, dried at 80°C for 15 minutes and

then cured at 170°C for 3 minutes. They were then repeatedly washed, dried and conditioned to constant weight. Physical strength properties including breaking strength, elongation, Elmendorf tear, inflated diaphragm abrasion and Monsanto wrinkle recovery angles were then determined in accordance with standard ASTM procedures. These test data are summarized in Table #2 together with similar data on analogously cross linked cotton fabrics without the polyethylacrylate polymer coatings.

Consideration of these experimental results shows that the methylolamide cross linked polyethylacrylate coated cotton fabrics exhibited quite substantial improvements in shape holding properties as indicated by Monsanto wrinkle recovery angle values even at low cross linking agent add-on's over a relatively wide range of polyethylacrylate loadings. Thus Monsanto wrinkle recoveries in the 280-300 range were obtained with 1-2% cross linking agent add-on's at between 3 to 20% ethylacrylate polymer deposits. The strength properties were however substantially reduced as was tear strength and abrasion resistance. The best results were obtained for 5-10% polymer deposits and 1-2% cross linking agent add-on's. They showed 280-300 Monsanto wrinkle recoveries with strength and abrasion resistance retentions in the order of 70%. These results are rather similar to those reported previously for a number of other methylolamide cross linked thermoplastic polymer coated cotton fabrics.

2. Glycidyl Methacrylate

The subsequent experiments relate to the free radical initiated vapor phase polymerization of glycidyl methacrylate monomer. As noted above, this monomer can be selectively polymerized either via the double bond or

the opening of the epoxide group leaving the other functional group intact for further reaction if so desired. Glycidyl methacrylate is an unusually versatile multifunctional monomer with high chemical reactivity. Sims⁽¹⁴⁾ of DuPont has noted that using a catalyst solution having pH of about 6 free radical homopolymerization of glycidyl methacrylate can take place essentially only via the vinyl group. Thus the epoxy group remains available for subsequent cross linking.

A 0.05M ceric-ammonium nitrate aqueous solution having a pH of about 3 was employed as catalyst in all the experiments conducted to encapsulate cotton fibers with polyglycidyl methacrylate. Infrared spectra of the homopolymer coated cloth samples using KRS-5 crystal did not show the presence of the epoxide group, even with sample containing as much as 30% polymer add-on. Silberman⁽¹⁵⁾ has found that ketones like acetone, methyl ethyl ketone dissolve uncrosslinked homopolymer of polyglycidyl methacrylate whereas effective solvents have as yet not been found for the crosslinked polymer. In the subsequently described experiments polyglycidyl methacrylate coated samples were subjected to soxhlet extraction using methyl ethyl ketone as the extractant. However, even after 70 hrs. of extraction weight measurements showed that polymer could not be extracted from the cloth samples suggesting that the polyglycidyl methacrylate was, indeed, crosslinked. Also, infrared spectrum of the extractant methyl ethyl ketone (after 70 hrs. of extraction) did not show the presence of the polymer.

Hot transport of glycidyl methacrylate monomer vapor to the polymerization chamber either per se or with an inert carrier gas as was done in case of ethyl acrylate, was found to be impractical because of the ease of polymerization of the liquid monomer at a temperature range as low as 80-90°C.

Hence all the experiments with glycidyl methacrylate had to be carried out at reduced pressure. Various other experimental attempts to avoid polymerization under reduced pressure such as mixing the glycidyl methacrylate monomer with low boiling miscible aromatic solvents or the formation of low boiling azeotropes with water proved to be unsatisfactory.

The following describes the details of the experimental procedure including the relations between different vapor exposure times, reaction temperatures, etc. to the polymer add-on obtained and also results present the Soxhlet extraction data obtained.

Typical studies on vapor phase coating of cotton
print cloth samples with polyglycidyl methacrylate

10" x 6" cotton samples were cut from mercerized, bleached 80 x 80 cotton print cloth. An aqueous solution of 0.05M ceric-ammonium nitrate was prepared by dissolving 27.5 gms of ceric-ammonium nitrate (Mol. wt. 548.23, obtained from Fisher Scientific Co.) in 1000 ml. of distilled water. The conditioned and weighed cloth samples were mounted in stainless steel frames and then immersed in the aqueous catalyst solution for 1 minute, then allowed to stand in air for 10 minutes.

The stainless steel frames with the catalyst impregnated cloth samples were then put inside a preheated vacuum oven. 3 aluminum cups containing 10 cc of glycidyl methacrylate monomer liquid were then also put inside the preheated vacuum oven. The system was then evacuated with a mechanical pump till a vacuum reading of 28.5" of Hg was read. The system was closed. Exposure time of the impregnated cotton cloth samples to glycidyl methacrylate monomer vapor were measured commencing with the time when the vacuum reading started to decrease.

After exposing the samples for predetermined times, the coated samples were taken out of the vacuum oven, washed in a stream of warm water (40-50°C) for 1/2 hr., dried in a forced air oven at 80°C for 1 hour and then conditioned for 1 hr. before the weights were recorded to get constant weights. From the difference in weights before and after exposure, the % gross-wt. gain were calculated. Data for typical selected runs are seen below in Tables #3 - #9.

Table #3. Polymerization reaction chamber (vacuum oven): 60°C

Vapor exposure time: 1 hr.

Immersion time of cloth samples in catalyst soln.: 1 min.

Sample Designation	Wt. of conditioned samples before exposure to vapor, (gms) (A)	Wt. of samples after exposure, washing, drying and conditioning, (gms) (B)	% gross-wt. gain $\frac{B-A}{A} \times 100$
#1	3.986	4.401	10.4
#2	4.014	4.417	10.1
#3	3.865	4.278	10.7
#4	3.828	4.231	10.5
#5	4.105	4.527	10.3
Gross av. wt. % gain			10.4 %

Table #4. Polymerization reaction chamber: 60°C

Immersion time of cloth samples in catalyst soln.: 1 min.

Vapor exposure time: 1/2 hr.

Sample Designation	Wt. of conditioned samples before exposure to vapor, (gms) (A)	Wt. of samples after exposure, washing, drying and conditioning, (gms) (B)	% gross-wt. gain $\frac{B-A}{A} \times 100$
#6	3.885	4.017	3.4
#7	4.019	4.155	3.4
#8	4.026	4.173	3.6
#9	3.881	4.021	3.6
#10	3.920	4.053	3.4
Gross av. wt. gain			3.5 %

Table #5. Polymerization reaction chamber: 60°C

Immersion time of cloth samples in catalyst soln.: 1 min.

Vapor exposure time: 1-1/2 hr.

Sample Designation	Wt. of conditioned samples before exposure to vapor, (gms) (A)	Wt. of samples after exposure, washing, drying and conditioning, (gms) (B)	% gross-wt. gain $\frac{B-A}{A} \times 100$
#11	4.074	4.718	15.8
#12	3.937	4.631	17.4
#13	3.887	4.510	16.0
#14	3.977	4.666	17.30
#15	4.076	4.757	16.70
Gross av. weight gain			16.7 %

Table #6. Polymerization reaction chamber: 60°C

Immersion time of cloth in catalyst soln.: 1 min.

Vapor exposure time: 2 hrs.

Sample Designation	Wt. of conditioned samples before exposure to vapor, (gms) (A)	Wt. of samples after exposure, washing, drying and conditioning, (gms) (B)	% gross-wt. gain $\frac{B-A}{A} \times 100$
#16	4.080	4.893	19.9
#17	4.085	4.932	20.8
#18	4.011	4.794	19.5
#19	4.115	4.946	20.2
#20	3.842	4.588	<u>19.4</u>
Gross av. wt. gain			20 %

Table #7. Polymerization reaction chamber: 80°C

• Immersion time of cloth samples in catalyst soln.: 1 min.

Vapor exposure time: 15 min.

Sample Designation	Wt. of conditioned samples before exposure to vapor, (gms) (A)	Wt. of samples after exposure, washing, drying and conditioning, (gms) (B)	% gross-wt. gain $\frac{B-A}{A} \times 100$
#21	4.165	4.353	4.5
#22	4.162	4.354	4.6
#23	3.947	4.124	4.5
#24	3.979	4.138	4.0
#25	4.015	4.196	<u>4.5</u>
Gross av. wt. gain			4.4 %

Table #8. Polymerization reaction chamber: 80°C

Immersion time of cloth samples in catalyst soln.: 1 min.

Vapor exposure time: 1/2 hr.

Sample Designation	Wt. of conditioned samples before exposure to vapor (gms) (A)	Wt. of samples after exposure, washing, drying and conditioning, (gms) (B)	% gross-wt. gain $\frac{B-A}{A} \times 100$
#25	4.152	4.612	11.1
#27	3.950	4.393	11.2
#28	3.937	4.335	10.1
#29	4.051	4.491	10.9
#30	3.997	4.433	<u>10.9</u>
Gross av. wt. gain			10.8 %

Table #9. Polymerization reaction chamber: 80°C

•Immersion time of cloth samples in catalyst soln.: 1 min.

Vapor exposure time: 1 hr.

Sample Designation	Wt. of conditioned samples before exposure to vapor (gms) (A)	Wt. of samples after exposure, washing, drying and conditioning, (gms) (B)	% gross-wt. gain $\frac{B-A}{A} \times 100$
#31	4.098	5.105	24.6
#32	4.088	5.128	25.4
#33	4.045	5.082	25.6
#34	4.062	5.089	25.2
#35	3.997	4.967	<u>24.2</u>
Gross av. wt. gain			25 %

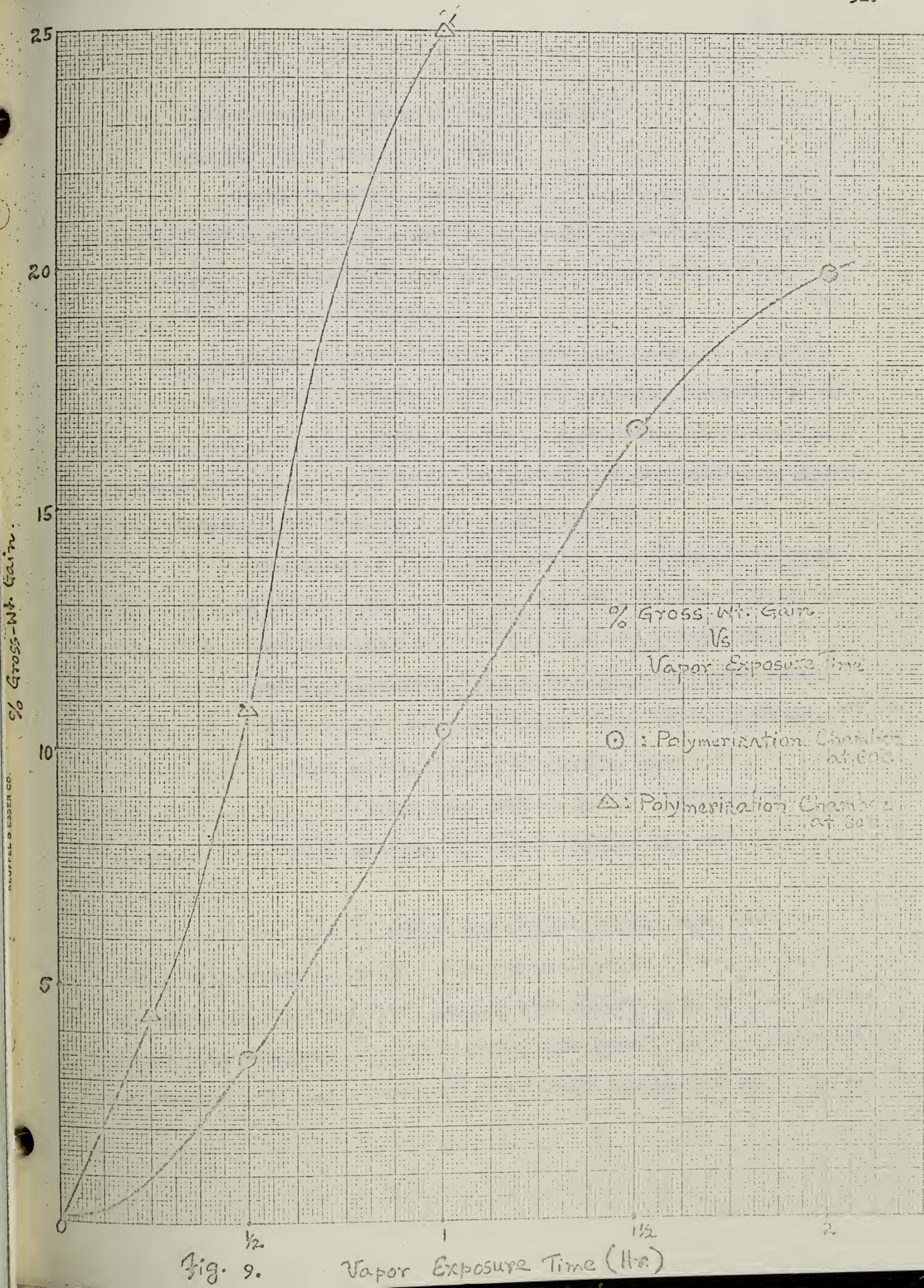
The data given in tables #3 - #9 have been plotted in Fig. 9. The % gross-wt. gain at a fixed temperature increases sharply as the vapor exposure time is increased. Also at a fixed exposure time, the % gross wt. gain increases as the temperature is increased.

Typical Soxhlet Extraction Studies:

The coated cloth samples were subjected to the soxhlet extraction with methyl ethyl ketone as the extractant. After 70 hrs. of extraction, the cloth samples were washed in a stream of warm water (40-50°C), dried at 80°C in a forced air oven for 2 hrs., allowed to equilibrate and weighed. Typical data are presented below:

Sample	Wt. of sample before extraction (gms) (A)	% Polymer add-on	Wt. of samples after extraction, washing, drying (gms) B	% gain in wt. $\frac{B-A}{A} \times 100$
# 1-A	4.386	16	4.421	0.8
# 2-A	4.688	17.8	4.726	0.8
# 3-A	4.239	10.7	4.278	0.9
Control	3.814	-	3.851	0.97

The small % gain in wt. in the last column of the above table is being investigated further. One possible explanation is exposure to humidity during weighing. (Note that this % gain in wt. is quite uniform).



3. Photomicroscopic studies of vapor deposited polymer coatings on cotton fibers

Photomicroscopic studies were initiated in order to help clarify physical character and structure of such polymer deposits on the cotton fibers. As indicated above the following problem areas were selected for special consideration:

- a) growth characteristics and degree of uniformity of polymer deposits,
- b) continuity of polymer coatings, c) physical situation prevailing at the so-called cross-over points (what happens to individual cotton fibers when they physically touch during polymer deposition and what happens to polymer coated fibers as they touch each other during growth).

Another area of interest related to the effects of varying polymer add-ons on both structure and the physical properties of polymer coated fibers and experiments were also conducted along these lines.

The equipment employed for these microphotographic studies consisted of a Wild binocular light microscope Model M-20 equipped with built-in tungsten light source, capable of magnification of 125, 500, and 1250, and facilities for taking both Polaroid and 35 mm photographs. An AO Spencer rotary type microtome was used for making cross-sections of fiber samples.

Two types of slides were prepared during these studies, namely 1) longitudinal section, and 2) cross sections. Photomicrographs of longitudinal uncoated fiber sections were compared with those of polymer coated fiber sections. The fiber samples were prepared by one of the following methods: (1) from the exposure of the fiber specimens to two or three

drops of cellulose solvent (1.00 molar cupriethylene diamine solution) for varying periods of time (30 sec. to 5 min.); (2) exposure of fiber specimens to an inert mounting medium (glycerine or mineral oil).

Fabric cross sectional samples were prepared by embedding following the Rohm and Haas suggested procedure⁽¹⁶⁾. The monomer of n-butyl methacrylate was used with dicumyl peroxide as the catalyst. Gelatin capsules served as molds in which specimens were placed and covered with catalyzed monomer. These capsules were heated to 80°C and kept at that temperature for two to three days to initiate and complete polymerization of the butyl methacrylate. All samples were cross-sectioned with the use of a Spencer microtome equipped with a specially designed capsule holder. Samples from 2 to 5 microns thick were prepared following this procedure and mounted in either glycerine or mineral oil for microscopic examination and study.

Much time was spent on investigations of various differential color staining techniques in order to visually distinguish the polymer coating from the cotton fiber substrate. A successful differential color staining technique would also aid significantly in establishing the precise boundary locations of the polymer deposits at different amounts of polymer add-ons. While a great number of different stains were experimentally investigated, the most success was obtained with a blue dispersion dye supplied by Geigy Chemical (Setacyl Blue-2GS conc. 250%), for the acrylic coatings. The fiber samples were stained by placing samples of the coated cloth in a water solution of this dye of pH 6.5-7.0 and heat to 200°F for 1-1/2 hours. The samples were then removed from the dyebath and washed under running water

for 3-4 hours. The thusly stained specimens were then embedded and cross-sectioned, as described above after which processing steps they were subjected to photographic examinations. Although the methacrylate embedding material did leach out some of the dye, generally enough color remained in the sample for differentiation. Improved staining procedures are under investigation.

Photomicroscopic studies were conducted on both polyethyl acrylate and polyglycidyl methacrylate polymer coated cotton fibers, polymerization having previously been effected from the vapor phase, as described in the earlier progress report. Since the softening point of PGMA is much higher than that of PEA, photomicrographs of PGMA coated cotton fibers can be more clearly investigated at ambient temperature conditions. While the subsequent discussion is illustrated with microphotographs of PGMA coated cotton fibers, the same phenomena have been observed with PEA coated cotton fibers under the microscope.

The black and white photomicrographs labeled figures 10, 11 and 12 are considered to furnish useful information on the character of the polymer deposits. The fiber samples shown in these photomicrographs were prepared as described earlier by exposure of the fiber specimens to the previously specified cellulose solvent for 5 minutes followed by photographic examination. This treatment dissolves the cellulose and keeps intact the enclosing polymer coating and shell.

Figure 10 at 500 x shows rather smoothly intertwined polymer shells or tubes of the sample with 2.7% gross polymer weight gain. These tubes are apparently quite uniform and seem to be transparent. Figure 11 at 500 x shows a single polymer tube of a sample with gross polymer weight gain 7.0%. This photo suggests that the ends of the tubes are at least partially open (even though the depth of field limitation of the microscope





Fig. 10 2.7% gross wt. gain
x 500

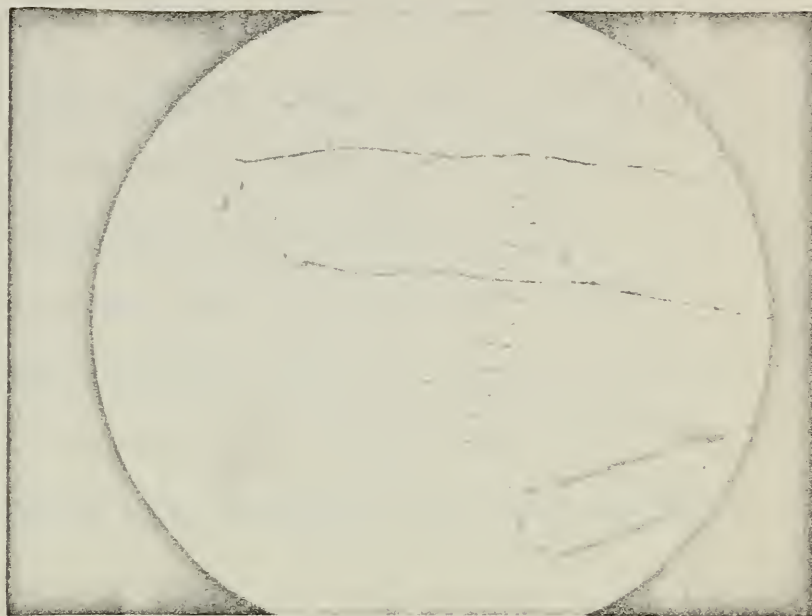


Fig. 11 7.0% gross wt. gain
x 500

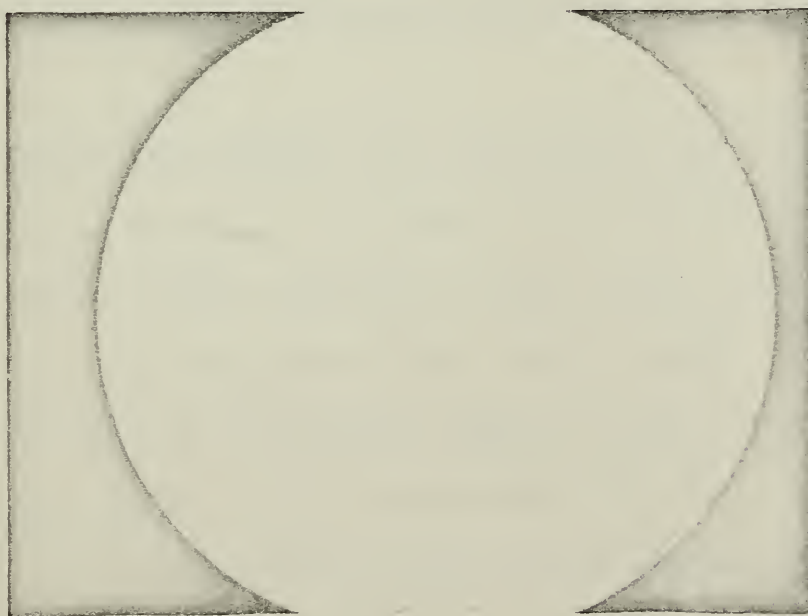


Fig. 12-11.5% gross wt gain
x 500

(10,11,12) all PCMA acetal cotton treated with cupriethylenediamine
to leave transparent tubes

makes it most difficult to properly focus on all planes of the tube causing the somewhat undistinct background). Figure (12) at 500 x shows tubes of yet another fiber sample with gross polymer weight gain of 11.5%. Information conveyed from this set of photos may be summed up as follows: Polymer tubes obtained after cellulose dissolution (the polymer having been deposited via the earlier discussed vapor phase polymerization methods employing PGMA monomer and a cotton fiber substrate) seem to be quite uniform, smooth, "continuous" and transparent in the region of polymer weight add-ons of approx. 2-12% with the added observation that the ends of the tubes appear to be at least partially open.

Figures (12) and (14) both taken at 125 x show similar information for a number of polymer tubes or shells. In the photomicrograph labeled (13) the tubes are essentially transparent the sample being exposed to cellulose solvent for 5 minutes. Figure (14) shows a sample exposed to solvent for only 30 sec. before being photographed. Some undissolved cellulose can be seen within some of the shells with impairment of transparency as might be expected.

Figures (15) through (19) are selected color photomicrographs prepared from 35 mm slides of a stained and cross-sectioned sample of PGMA polymer coated cotton cloth with a gross weight gain in excess of 30%. The advantage of using such high polymer add-on samples is the more ready color differentiation of the polymer deposit and the cotton substrate. These high weight gain samples do show interesting information regarding the physical structure and location of the polymer coatings and especially regarding the problem of the so-called cross over points. The blue colored portions indicate the dye stained plastic coatings in these pictures.



Fig. 13. PGMA tubes - cellulose complete dissolved
x 125

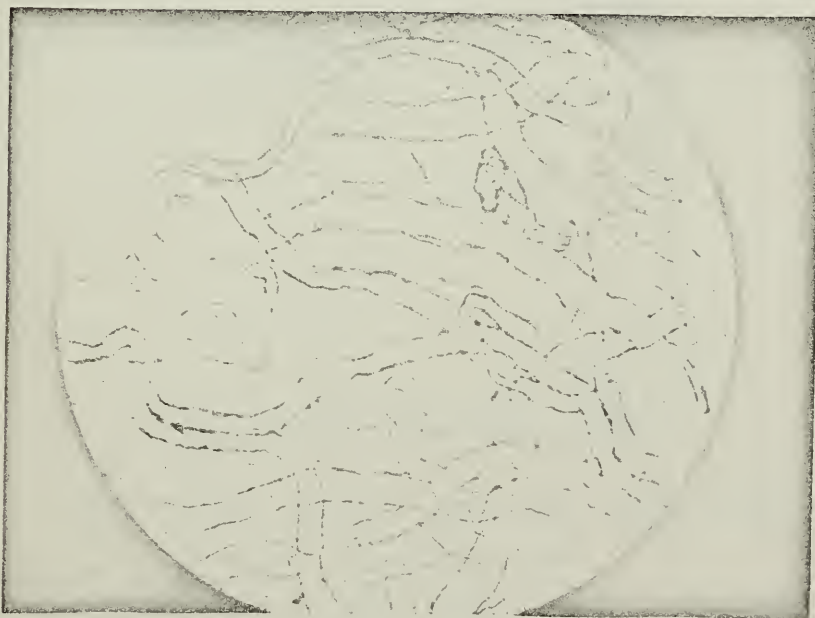


Fig. 14. PGMA tubes - cellulose partially dissolved
x 125



Fig. 15 x 125



Fig. 16 x 500

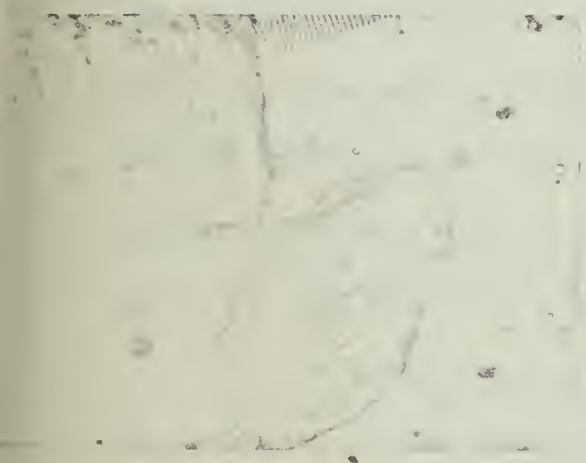


Fig. 17 x 1250

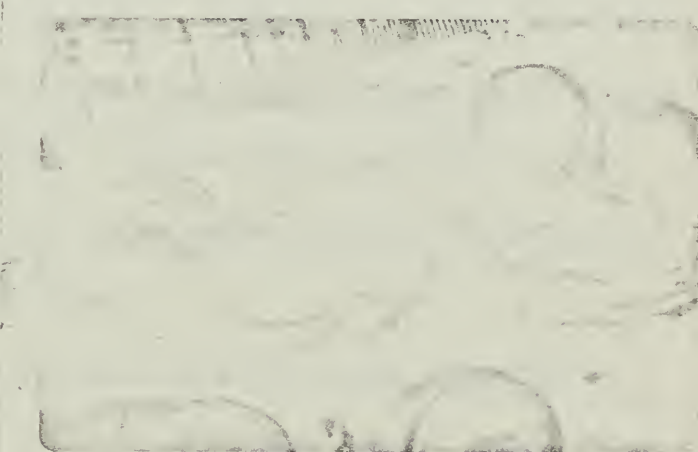


Fig. 18 x 1250

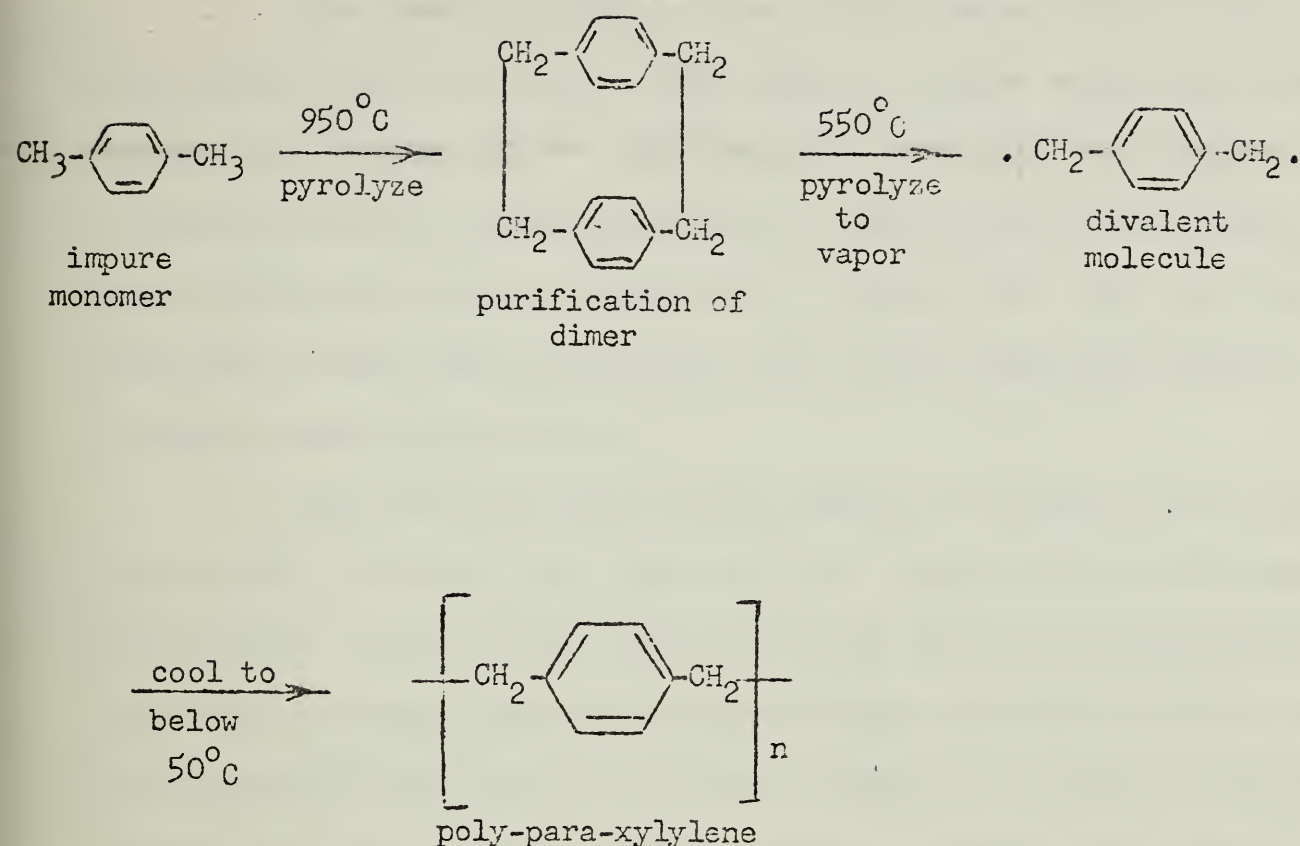


All photos of PGMA coated cotton, gross wt. gain > 20%;
 polymer stained with Geigy dispersion dye
 (Setacyl Blue - 2 GS conc. 250%)

Fig. 19 x 1250

Figure (15) shows a fiber which during embedment, has been caused to separate partially into individual fibrils. At the low power of 125x, only "hints" of blue stain are seen and the existence of a cross over point is clearly suggested. Figure (16) at 500x depicts well the relative "unevenness" of polymer growth at the 30% add-on level. In the upper left hand corner a polymer "weld" or cross-over point is seen. Figures (17), (18) and (19) at 1250x show both cross over points and "unevenness" of polymer growth more clearly. Figure (17) shows two fibril cross sections and illustrates particularly well the phenomenon of uneven polymer growth at the 30% add-on level. Figures (18) and (19) are two additional photos showing the location of a polymer weld or "cross-over" point at this high level of polymer add-on.

It was felt of interest to show that the above described observations did not only apply to the so-called high weight gain samples of PGMA polymer. A comparison is therefore made with a polymer coating on cotton fibers obtained from a completely different vapor phase coating system, namely poly-para-xylylene. This unique UCC developed coating system is summarized as follows: p-xylene (monomer) is pyrolyzed at about 950 °C in the presence of steam yielding the intermediate di-p-xylylene; the dimer is then purified and subsequently pyrolyzed at 550°C to yield a gaseous monomer which is a divalent molecule; polymerization of the monomer occurs instantaneously upon cooling to below 50°C. The resulting polymer poly-para-xylylene is linear and highly crystalline. Pictorially this reaction sequence is shown as follows: (17)



This vapor phase polymerization occurs on essentially any substrate being only temperature dependent. Thus coatings can be readily also produced on cotton fibers, for example. This system represents an excellent example of polymer encapsulation with no possibility of grafting etc. since the only processes taking place are condensation of the monomer vapor followed by its immediate polymerization (note no catalyst is employed). When a fiber substrate is used, the polymer forms on all exposed fiber surfaces forming a continuous sheath or tube around each exposed fibril. It is especially useful for studying the effects of various amounts of polymer add-on on both structure and physical properties of the fibers.

Six photomicrographs, three of poly-para-xylylene (about 50% gross weight gain) and three of PGMA (about 30% gross weight gain) are compared (photographs (20) - (25) inclusive.) They all show longitudinal sections prepared as discussed earlier by mounting the coated fiber in an inert medium (glycerine or mineral oil). Figures (20, (22), and (24) show PGMA coated cotton fiber while (21), (23) and (25) represent poly-p-xylylene coated cotton fiber.

The photos in this set are matched for comparison as follows: (20) and (21), (22) and 23), (24) and (25). Photos (20) and (21) and (22) and 23) - each at 125x - show on a gross scale the similarity of appearance between the two different polymer coatings for four different scenes. Note especially the existence of uneven "clumps" of polymer or incipient densities for both types of polymer coatings. Figures (24) and (25) at 500x show single fibrils separated from the bundle. The similarity of physical appearance at this higher magnification is still rather striking. The development of random clumps or incipient dendrites are clearly visible.

Consideration of the above photographs suggests a two step tube growth mechanism which is probably applicable to many other deposition processes on substrates. The initial growth phase appears to be essentially substrate surface controlled and the polymer deposits are relatively continuous and smooth. After a certain amount of build-up, the deposition becomes progressively less surface controlled and increasingly irregular growth takes place. The previously referred to rather random clumps or "dendrites" of polymer began to form with increasing frequency. The polymer add-on range at which this transition occurs will depend primarily on the

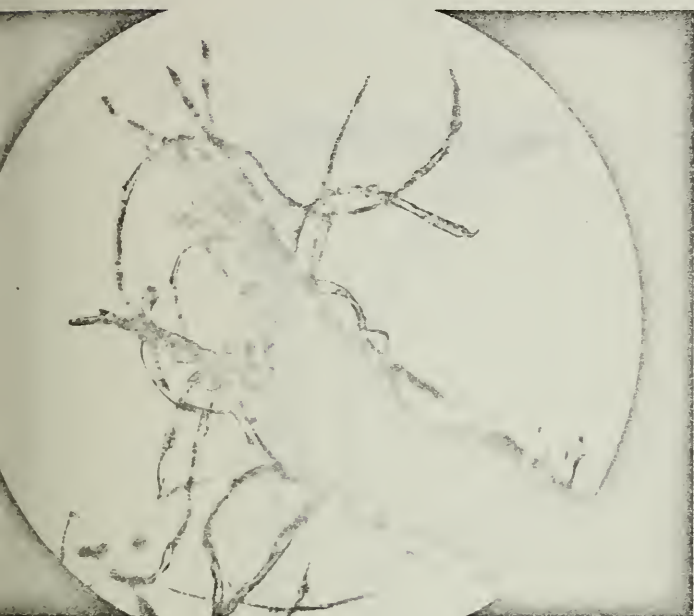


Fig. 20. PEMA coated cotton
x 125

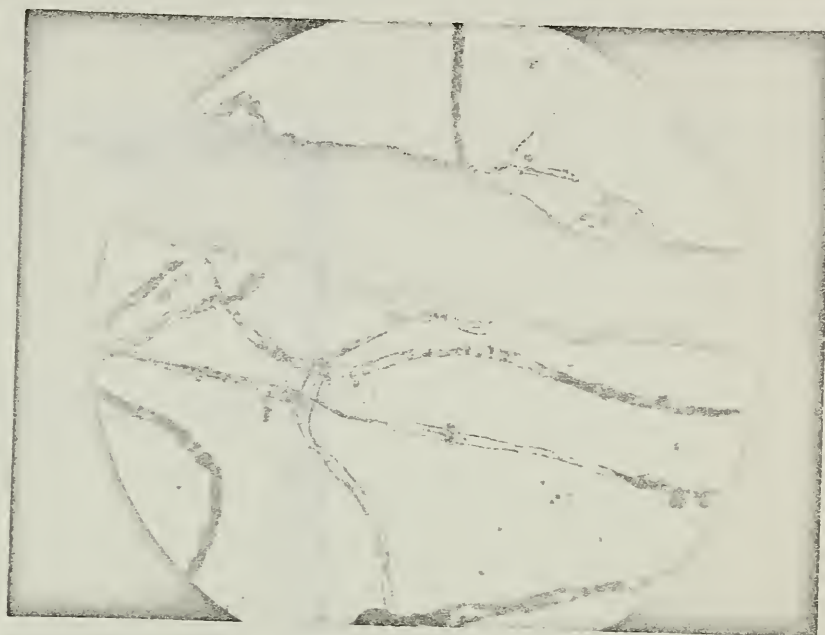


Fig. 21. Para xylylene coated cotton,
x 125



Fig. 22. PGMA coated cotton
x 125



Fig. 23. Para xylylene coated cotton
x 125



Fig. 24. PGMA coated cotton
x 500

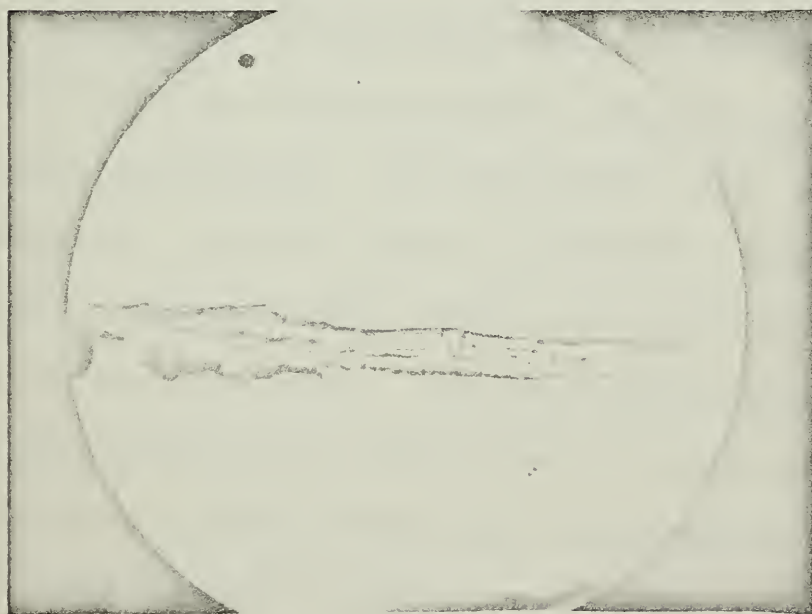


Fig. 25. Para xylene coated cotton
x 500

physical characteristics and geometry of the substrate and will be rather independent with respect to the particular type of polymer deposited.

Similar phenomenae have been observed in organic surface coatings from solution and also in metal electroplating systems.

B. Polyoxymethylene

This section deals with the development of a formaldehyde monomer based vapor phase polymerization system comprising the exposure of suitable catalyzed cotton cloths to purified formaldehyde vapor which then polymerizes to high molecular weight polyoxymethylene even at ambient temperatures selectively onto the catalyzed surfaces. High molecular weight polyoxymethylene polymer deposits were obtained by immersion of cotton fabrics in a suitable alkaline catalyst solution at ambient temperatures and in air and then exposing the catalyzed cloths to monomeric formaldehyde vapor. The time lag between the catalyst immersion and formaldehyde vapor exposure was not critical and amounted to between 7-10 minutes for many experiments. A typical catalyst system consisted of tributylamine and diphenylamine* dissolved in a halogenated solvent such as carbon tetrachloride. The formaldehyde vapor was generated by heating a paraformaldehyde - paraffin slurry at 115-120°C. It was carried in dry nitrogen gas to a polymerization chamber the experimental details of which system will be described below. Polyoxymethylene polymer coatings were deposited on the surface of the cotton fiber in amounts depending upon such reaction variables as formaldehyde vapor concentration, reaction time, temperature etc. Polymer deposits ranging from as little as 2% to over 50% based upon the weight of the cotton fabrics could be reproducibly obtained by

* antioxidant

varying reaction conditions. Typically 10% polymer add-on's could be obtained in approximately 10 minutes exposure time with one rather convenient set of reaction conditions.

As is well known polyoxymethylenes require end capping in order to enhance their thermal stabilities etc. This was accomplished by reacting the polyoxymethylene hydroxyl groups with acetic anhydride which treatment apparently decreased the solubility of the cotton fibers in cupriethylene-diamine. Typical end capping conditions were heating the polymer coated cotton fabrics in acetic anhydride solutions at 1140°C for approx. 30 minutes employing sodium acetate to catalyze the esterification. Experiments with selected difunctional and polyfunctional anhydrides are planned in order to attempt cellulose cross linking as well as end capping.

The uncapped polyoxymethylene polymer deposits were isolated by solvent extraction in hot dimethylformamide, precipitated at ambient temperatures, purified by washing etc., dried in vacuo and identified by infrared and chemical analyses. Melting points and molecular weight determinations were also carried out. Experiments were also conducted involving dissolution of the cellulose in cupriethylenediamine solvent leaving behind shells of polyoxymethylene polymer. Similar solvent extraction studies were carried out on end capped polyoxymethylene coated fabrics except that cellulose solution in cupriethylenediamine was much reduced. Photomicrographic studies were carried out in order to ascertain the location of these polymer deposits on the fibers. Differential staining of cross section of fiber specimens show that the polymer deposits are located along the outer periphery of the fibers.

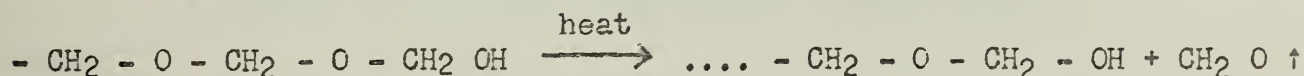
Physical strength measurements have been made on such polyoxymethylene polymer modified cotton fibers and are continuing. Preliminary results on numerous test samples show no loss in tensile strength and tear resistance, improved elongation and enhanced abrasion resistance over a large range of polymer loadings. These results compare favorably with acid catalyzed formaldehyde cotton treatments which generally result in substantial losses in the strength properties of cotton fabrics.

Formaldehyde alone and in the form of various reactive adducts such as, for example, the dimethylol ureas, carbamates, triazones etc. have been widely used to modify the properties of cotton fabrics⁽¹⁸⁾. The effectiveness of these treatments varies widely depending on many factors such as the type and amount of the compound employed, the severity of the reaction conditions, modifying additives etc. In many cases wrinkle recovery crease retention etc. can be improved with cross linking of the cellulose cotton at the expense of breaking strength, tear and abrasion resistance. A very considerable amount of research and development has been initiated and is in progress in order to obtain what have been loosely called "permanent press" treated cotton fabrics with an improved balance of properties, particularly so as regards tear strength, abrasion resistance and smooth drying. The loss in certain important physical properties associated with the strength and durability of such variously treated cotton fabrics may be related to the nature of the generally acidic catalysts which attack the cellulose.

The high molecular weight polyoxymethylene polymers and copolymers produced commercially by companies such as DuPont and Celanese have apparently not been considered as cotton treating agents and/or modifiers. The

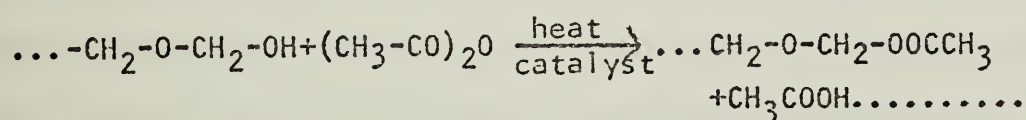
outstanding chemical and physical properties of these plastics are well known and increasingly employed in industry. It is of interest that experimental conditions are known which permit preparation of such macromolecular materials at relatively mild conditions employing catalyst systems which do not affect the strength properties etc. of cotton cellulose adversely. Experiments were therefore carried out on the vapor phase polymerization of formaldehyde monomer selectively onto suitably catalyzed cotton fabrics in the hope of minimizing the undesirable effects frequently associated with formaldehyde cotton treatments while developing improved tear strength, abrasion resistance and other wanted cotton fiber improvements. Polyoxymethylene homopolymer modified cottons have not been reported in the literature. For the polymerization of formaldehyde, the preparation and purification of the formaldehyde monomer are essential problems. Methanol formic acid, and water are the usual contaminants in the pyrolysis of paraformaldehyde, and cause undesirable premature polymerization leading to water soluble low molecular weight polymers. These materials must be removed from the monomer one convenient way being by condensation in cold traps, as will be discussed later. High purity, very dry formaldehyde monomer is essential for the preparation of high molecular weight polymers.

Although the newer types of polyoxymethylene polymers in use today are quite stable thermally, end capping of their residual hydroxyl end groups is necessary in order to retard depolymerization or "unzippering" especially at high temperatures a reaction resulting in the steady evolution of formaldehyde gas as shown below:



The hydroxyl end-groups can be esterified, etherified, or can be reacted with compounds such as α -chloro alkylethers, epoxides. The esterified or etherified products block depolymerization from the chain ends and hence, increase polymer stability still further with littler or no effect on the fundamental properties of the base polymer. Modification of the hydroxyl end-groups by esterification, etc., is commonly known as end-capping. Typical end-capping reactions can be represented as follows:

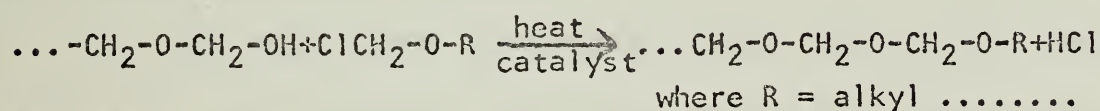
(1) Esterification with acetic anhydride:



(2) Etherification with alcohols:



(3) Reaction with -chloroalkylethers:



(4) Reaction with epoxides:



The subsequent experimental studies were concerned with the application of one of these end capping treatments of the vapor deposited polyoxymethylene coatings, namely esterification with acetic anhydride.

A summary of pertinent experimental conditions etc. follows.

Experimental Details

Materials:

Fabric: The fabrics employed throughout this part of the study were 80 x 80 desized, bleached, mercerized cotton print cloths. 10" x 6" fabric samples were cut from 80 x 80 print cloths for use in the subsequently described vapor phase polymerization studies.

Chemicals: The specific polymerization catalyst used in this study was prepared by dissolving 7.5 cc of tri-n-butylamine (obtained from Eastman Organic Chemicals, Rochester, N.Y.) and 3.6 g. of diphenylamine (obtained from Fisher Scientific Co.) in 1500 ml. of carbon tetrachloride. A slurry of paraformaldehyde in paraffin oil was prepared by mixing thoroughly 75 g. of paraformaldehyde (obtained from Fisher Scientific Co.) with 300 ml. of paraffin oil in a half-liter resin kettle.

Vapor Phase Encapsulation Process:

The vapor phase encapsulation unit used in this work consisted of a 8" x 8" x 12" stainless steel lined vacuum oven which acted as the polymerization chamber. This oven can be used for vacuum as well as for pressure work by using appropriate gaskets. The cloth samples were mounted on stainless steel frames which were then suspended inside the polymerization chamber from a rack, also constructed of stainless steel. A second chamber consisted of a half-liter Pyrex resin kettle which was jacketed with an electrical heating mantle. This kettle contained a paraformaldehyde-paraffin oil slurry from which the formaldehyde vapors were generated by heating to 115-120°C. The monomer was carried in dry nitrogen gas.

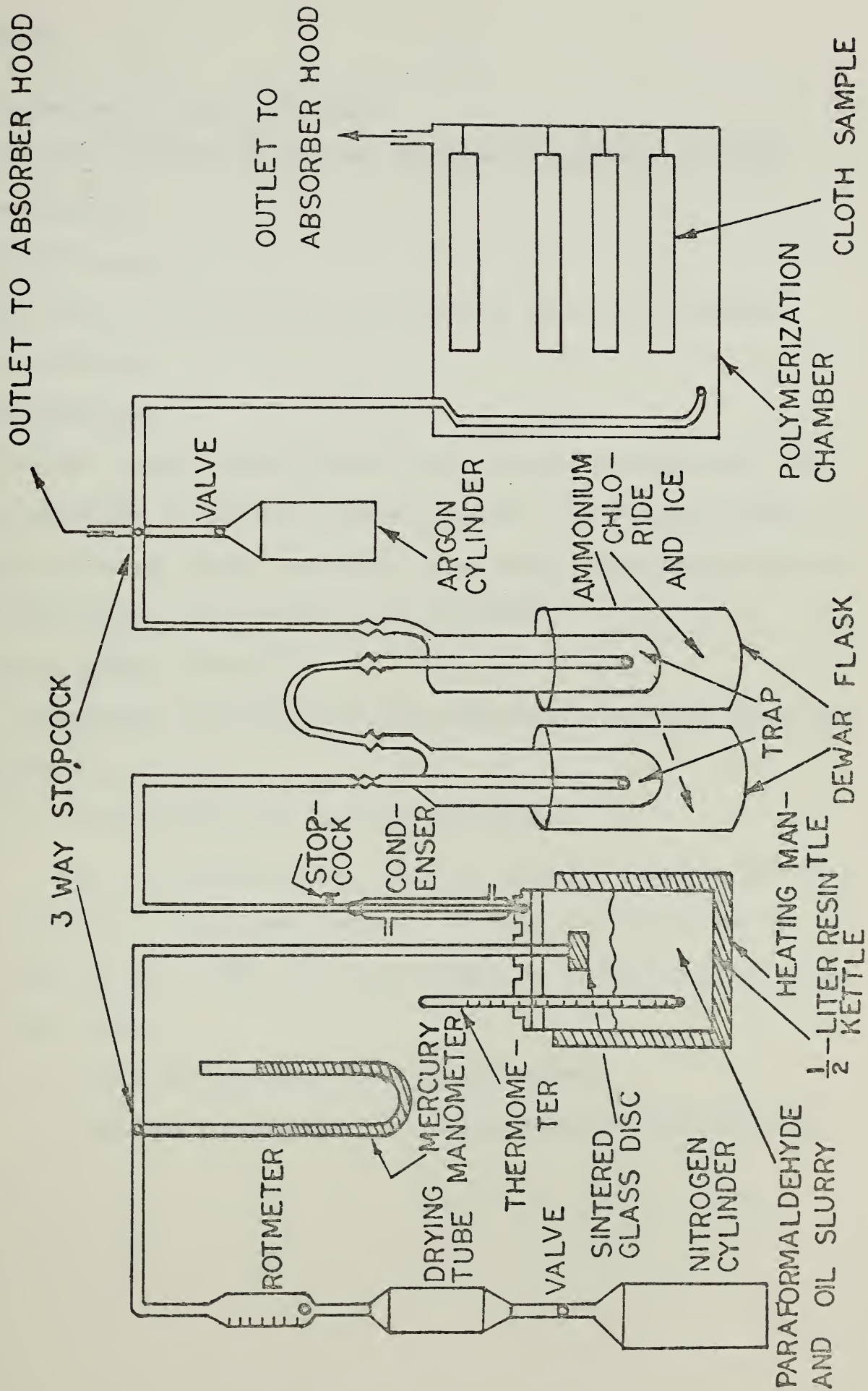
Because - as noted - methanol, formic acid, and water - the usual by products from the pyrolysis of paraformaldehyde - cause undesirable premature polymerization leading to the water soluble low molecular weight polymers, the nitrogen-formaldehyde gas stream was first passed through two traps, cooled to -15 -- -17°C by ammonium chloride + ice, to condense the above mentioned undesirable by products.

Suitably conditioned cloth samples were impregnated with the catalyst by immersing in catalyst solution. The time between immersion in the catalyst solution and exposure to the formaldehyde monomer was not critical amounting typically to between 7-10 minutes. The samples were then suspended inside the polymerization chamber, which was flushed out by argon gas in order to displace air. The purified nitrogen-formaldehyde gas stream was directed into the chamber to cause polymerization of the purified formaldehyde vapor onto the surfaces of the catalyst activated cotton cloth samples. The excess reagent gas leaving the polymerization chamber was condensed in a cold trap. Equipment details etc. are shown in Fig. 26.

For purposes of this investigation, the nitrogen gas flow rate (0.9 liters/min.), slurry temperature (115 - 120°C), catalyst concentration, immersion time of the cloth samples in the catalyst solution (1 min.), polymerization chamber temperature (25°C) were kept constant. The exposure time of the catalyst activated cloth samples to monomer formaldehyde vapor were varied in order to obtain different polymer add-ons and study their effect on pertinent physical and chemical properties of the cotton samples.

FIG. 26. SCHEMATIC DIAGRAM OF VAPOR

PHASE COATING OF COTTON
CLOTH WITH POLYOXYMETHYLENE



Test Methods

1) Determination of % gross wt. gain:

The same procedure as has been described in previous progress report was followed.

2) Breaking Strength:

The same procedure as has been described in previous progress report was followed.

3) Wrinkle Recovery:

The dry wrinkle recovery values were measured following the same procedure described in previous progress reports. For the measurement of wet wrinkle recovery values, the coated cloth samples were treated with an aqueous 0.1% Triton X solution for 5 min. at 150°F.

4) Photomicrographic Studies:

(1) Longitudinal views of fibers were observed in the same way as has been described previously.

(2) a. Differential Color Staining Procedure:

The differential color staining procedure described previously was also employed in this investigation. The same blue dispersion dye (i.e., Setacyl Blue-2GS conc. 250%) was used to stain the polyoxymethylene coated cotton cloth samples.

(2) b. Method for Preparing Fiber Cross-Sections:

Identical chemicals and procedure described previously were employed.

5) End-Capping Procedure:

The end-capping of the deposited polyoxymethylene was carried out by treating the polymer coated cloth samples with acetic anhydride at 110°C for 30 minutes. The anhydride treated samples were then washed, dried, and conditioned, before taking the weight measurements.

6) Solvent Extraction Studies:

The procedure previously described in the previous progress report was followed, with the following modifications:

(a) For Polyoxymethylene coated cloth samples:

Extractant: Dimethylformamide

Time of Extraction: 2 hours

(b) For "End-Capped Polyoxymethylene" coated cloth samples:

Extractant: Dimethylformamide

Time of Extraction: 6 hours

Preliminary extraction studies showed that these extraction periods were sufficient to completely remove the homopolymers from the cloth substrates.

7) Identification of Polymer:

Polyoxymethylene and "end-capped" polyoxymethylene polymers were identified by taking infrared spectra of the films made of the dimethylformamide extracted polymers. On cooling below 110°C , the extracted polymer precipitates out from the dimethylformamide solution. The precipitated polymers were filtered, washed several times with acetone and, then, with ether, followed by drying under vacuum at 50°C . Thin films of polymers were made by pressing a small amount of polymer at 90° in a laboratory press.

8) Abrasion Resistance (Flex): ASTM-D1175-64T.

The procedure described in previous progress reports was followed.

9) Tearing Strength:

ASTM: 1424-63 (Elmendorf tearing strength) method was used.

10) Melting Point of Polyoxymethylene:

The polymer melting point was measured in the "Fisher-John Melting Point Apparatus".

11) Number Average Molecular Weight of Polyoxymethylene (\bar{M}_n):

The number average molecular weight of polyoxymethylene was calculated from the following three steps:

(a) The relative viscosity of polyoxymethylene was determined in a viscometer utilizing a 0.5% solution of polyoxymethylene at 60°C in p-chlorophenol containing 2% by weight of alpha-pinene.

(b) The inherent viscosity was calculated from the following equation

$$\text{Inherent Viscosity} = \frac{\ln \text{relative viscosity}}{C}$$

$$\text{where: relative viscosity} = \frac{\text{solution viscosity}}{\text{solvent viscosity}}$$

$$C = \text{concentration of solute in solution} \\ (\text{gram of polymer}/100 \text{ ml. of solution})$$

$$(c) \text{ Inherent Viscosity} = 3.82 \times 10^{-4} \bar{M}_n (0.83)$$

Experimental Results and Discussion

Experimental investigations of the vapor phase deposition of polyoxymethylene homopolymer onto catalyst impregnated cotton fabrics via tri-n-butylamine and diphenylamine catalyst included studies of the following experimental variables:

- (a) Monomer vapor exposure time,
- (b) Amount of polymer "add-on" (i.e., % gross wt. gain of cloth samples).

Vapor phase polymerization data are presented in Tables 10 - 16 and are plotted in Fig. 27. Soxhlet extraction studies of deposited polyoxymethylenes on cotton cloth substrates are shown in Table 17. Selected physical test data on the polymer coated cottons are shown in Table 18.

Photomicrographs (longitudinal view) of polyoxymethylene coated samples treated with cupriethylenediamine solvent are presented in Figs. 28, 29, 30 and 31. Fig. 32A,B,C,D show photomicrographs prepared from 35 mm. slides of stained and cross-sectioned samples (12% ~ 50% wt. gain) of polyoxymethylene coated cloth.

Typical infrared spectra of polyoxymethylene and "end-capped" polyoxymethylene films are given on Figs. 33 and 34 respectively.

Table 10. Vapor Phase Polymerization of Formaldehyde
Monomer Vapor onto Cotton Cloth Samples

Polymerization reaction chamber: 25°C
Immersion time of cloth samples in catalyst soln.: 1 min.
Vapor exposure time: 5 min.

Sample Designation	Initial cloth sample wt. (a), g.	Wt. of cloth samples after monomer vapor exposure, washing, drying & conditioning, (B), g.	% gross wt. gain $\frac{B-A}{A} \times 100$
#1	4.071	4.114	1.8
#2	3.994	4.096	2.5
#3	4.078	4.180	2.5
#4	3.902	3.988	2.2
#5	3.698	3.772	2.0
#6	3.649	3.724	2.0
#7	3.678	3.755	2.1
#8	3.688	3.766	2.1
#9	3.870	3.944	1.9
#10	3.888	3.954	1.7
#11	3.658	3.725	1.8
#12	3.825	3.891	1.7

Avg. % gross wt. gain: 2.0

Table 11. Vapor Phase Polymerization of Formaldehyde
Monomer Vapor onto Cotton Cloth Samples

Polymerization reaction chamber: 25°C
Immersion time of cloth samples in catalyst soln.: 1 min.
Vapor exposure time: 7.5 min.

Sample Designation	Initial cloth sample wt. (A), g.	Wt. of cloth samples after monomer vapor exposure, washing, drying & conditioning, (B), g.	% gross wt. gain $\frac{B-A}{A} \times 100$
#13	3.903	4.033	3.3
#14	3.958	4.115	3.9
#15	3.850	4.001	3.9
#16	4.056	4.215	3.9
#17	3.773	3.905	3.5
#18	3.817	3.940	3.2
#19	3.796	3.940	3.8
#20	3.719	3.842	3.3
#21	3.884	4.001	3.0
#22	3.846	3.957	2.9
#23	3.859	3.975	3.0
#24	3.766	3.916	4.0

Avg. % gross wt. gain: 3.48

Table 12. Vapor Phase Polymerization of Formaldehyde
Monomer Vapor onto Cotton Cloth Samples

Polymerization reaction chamber: 25°C
Immersion time of cloth samples in catalyst soln.: 1 min.
Vapor exposure time: 10 min.

Sample Designation	Initial cloth sample wt. (A), g.	Wt. of cloth samples after monomer vapor exposure, washing, drying & conditioning, (B), g.	% gross wt. gain $\frac{B-A}{A} \times 100$
#25	3.872	4.096	5.8
#26	4.114	4.351	5.7
#27	3.834	4.044	5.5
#28	3.859	4.054	5.0
#29	3.825	4.034	5.5
#30	4.036	4.246	5.2
#31	3.822	4.034	5.5
#32	3.800	3.992	5.0
#33	3.885	4.132	6.3
#34	3.918	4.109	4.9
#35	3.800	4.034	6.1
#36	3.854	4.093	6.2

Avg. % gross wt. gain: 5.5

Table 13. Vapor Phase Polymerization of Formaldehyde Monomer
Vapor onto Cotton Cloth Samples

Polymerization reaction chamber: 25°C
 Immersion time of cloth samples in catalyst soln.: 1 min.
 Vapor exposure time 15 min.

Sample Designation	Initial cloth sample wt. (A), g.	Wt. of cloth samples after monomer vapor exposure, washing, drying & conditioning, (B), g.	% gross wt. gain $\frac{B-A}{A} \times 100$
#37	3.794	4.127	8.8
#38	3.943	4.279	8.5
#39	4.054	4.413	8.8
#40	3.895	4.251	9.1
#41	3.861	4.168	8.0
#42	4.051	4.401	8.6
#43	3.822	4.166	9.0
#44	3.677	4.017	9.2
#45	4.086	4.505	10.2
#46	4.096	4.526	10.7
#47	3.817	4.224	10.6
#48	3.877	4.264	10.0

Avg. % gross wt. gain: 9.3

Table 14. Vapor Phase Polymerization of Formaldehyde
Monomer Vapor onto Cotton Cloth Samples

Polymerization reaction chamber: 25°C
 Immersion time of cloth samples in catalyst soln.: 1 min.
 Vapor exposure time: 20 min.

Sample Designation	Initial cloth sample wt. (A), g.	Wt. of cloth samples after monomer vapor exposure, washing, drying & conditioning, (B), g.	% gross wt. gain $\frac{B-A}{A} \times 100$
#49	3.934	4.440	12.9
#50	3.937	4.462	13.3
#51	3.863	4.415	14.3
#52	3.823	4.349	13.7
#53	3.723	4.233	13.7
#54	3.945	4.487	13.7
#55	3.772	4.268	13.1
#56	3.791	4.334	14.3
#57	3.919	4.492	14.6
#58	3.891	4.369	12.3
#59	3.880	4.439	14.4
#60	3.876	4.441	14.6

Avg. % gross wt. gain: 13.7

Table 15. Vapor Phase Polymerization of Formaldehyde Monomer
Vapor onto Cotton Cloth Samples

Polymerization reaction chamber: 25°C
 Immersion time of cloth samples in catalyst soln.: 1 min.
 Vapor exposure time: 25 min.

Sample Designation	Initial cloth sample wt. (A), g.	Wt. of cloth samples after monomer vapor exposure, washing, drying & conditioning, (B), g.	% gross wt. gain $\frac{B-A}{A} \times 100$
#61	3.801	4.471	17.6
#62	3.975	4.658	17.2
#63	3.838	4.462	16.2
#64	3.733	4.427	18.6
#65	3.843	4.555	18.5
#67	3.874	4.535	17.0
#68	4.011	4.711	17.5

Avg. % gross wt. gain: 17.6

Table 16. Vapor Phase Polymerization of Formaldehyde Monomer
Vapor onto Cotton Cloth Samples

Polymerization reaction chamber: 25°C
 Immersion time of cloth samples in catalyst soln.: 1 min.
 Vapor exposure time: 30 min.

Sample Designation	Initial cloth sample wt. (A), g.	Wt. of cloth samples after monomer vapor exposure, washing, drying & conditioning, (B), g.	% gross wt. gain $\frac{B-A}{A} \times 100$
#69	3.820	4.655	21.8
#70	3.763	4.479	19.0
#71	3.805	4.589	20.6
#72	3.996	4.764	19.2
#73	4.007	4.893	22.1
#74	3.792	4.527	19.4
#75	3.752	4.653	24.0
#76	3.896	4.854	24.6
#77	3.809	4.557	19.2
#78	3.974	4.953	24.6

Avg. % gross wt. gain: 21.4

Table 17. Soxhlet Extraction Studies of Deposited Polyoxymethylene

on Cotton Cloth Substrates

Sample Designation	Initial Cloth sample wt., g. (A)	Wt. of coated sample before extraction, g. (B)	% gross wt. gain $\frac{B-A}{A} \times 100$	Wt. of sample after extraction, washing, drying and conditioning, g. (C)	% of gross wt. gain as graft polymer $\frac{C-A}{A} \times 100$
Control	3.885	-	-	3.815	-
Control	3.911	-	-	3.835	-
Control	3.842	-	-	3.769	-
#11	3.658	3.725	1.8	3.588	-
#24	3.766	3.916	4.0	3.721	-
#48	3.877	4.264	10.0	3.801	-
#78	3.974	4.953	24.6	3.898	-

TABLE 18. Physical Properties of Polyoxymethylene Coated Cotton Cloth Samples

Sample designation	% wt. gain (a)	Breaking strength, lb (b)			Tearing strength, g (c)	Abrasion (flex) resistance cycles-failure (d)
		Warp	Fill	% elongation		
Control	-	5.8	58.7	17.4	470	87
#1-C	-	8.5	63.4	20.1	578	74
#2-C	2.0	8.0	60.6	20.8	588	90
#3-C	5.5	7.4	60.1	20.9	590	119
#4-C	9.3	7.4	56.6	20.3	552	125
#5-C	14.7	7.1	61.5	19.1	540	153
#6-C	24.0	6.3	66.2	16.3	432	194

Note: Sample #1-C: Control treated with acetic anhydride at 140°C for 30 min. Sample did not gain any weight.
 (a): Avg. value of 8 samples. The coated samples were treated with acetic anhydride at 140°C for 30 min.
 (b): Avg. value of 5 runs.
 (c): Avg. value of 4 runs.
 (d): Avg. value of 3 runs.

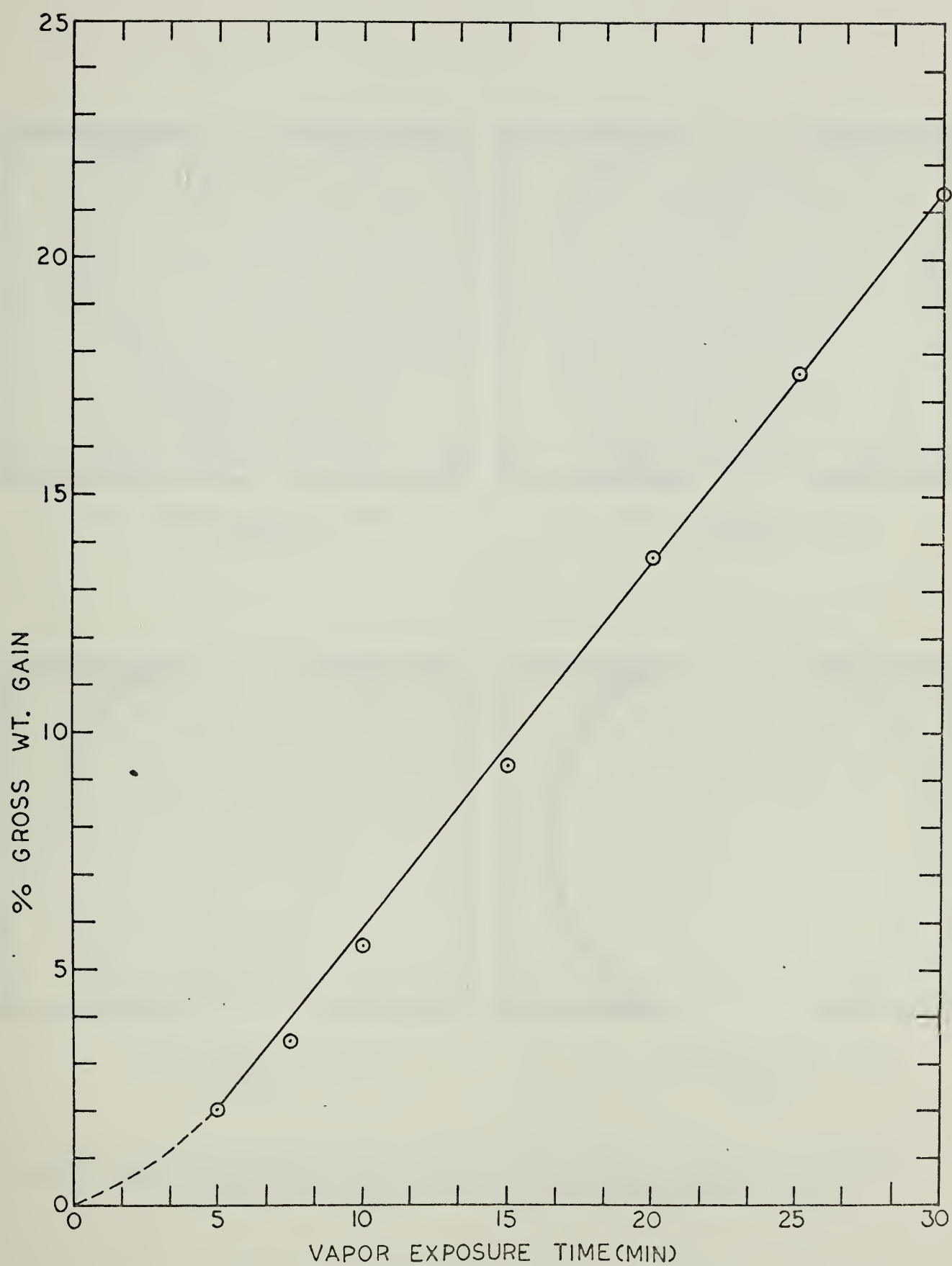
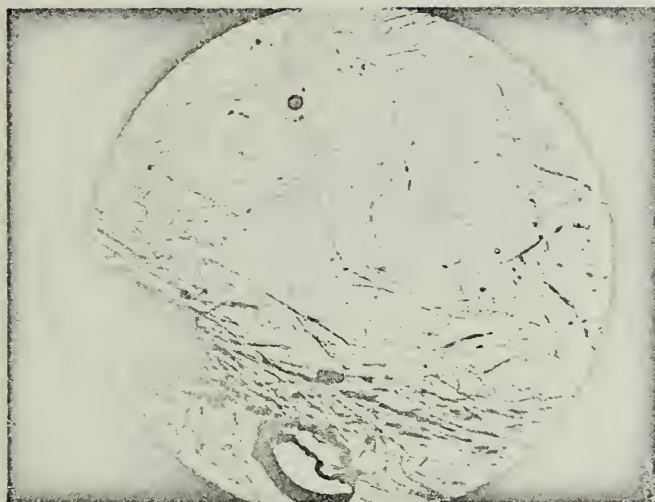


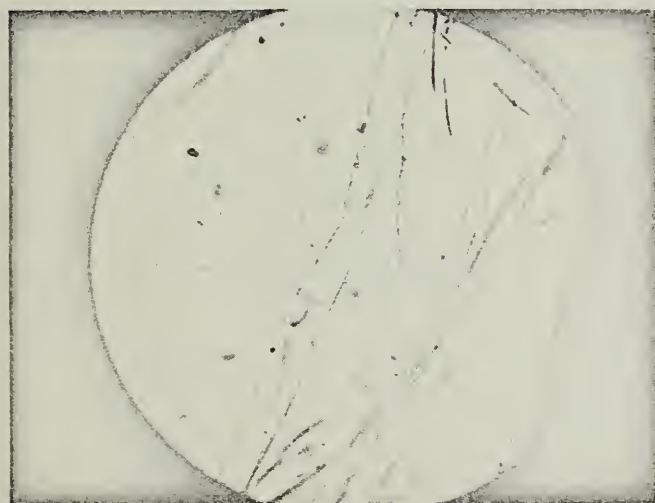
FIG. 27. % GROSS WT. GAIN VS. VAPOR EXPOSURE TIME



A. 6.2% gross wt. gain
X 125



B. 6.2 % gross wt. gain
X 125

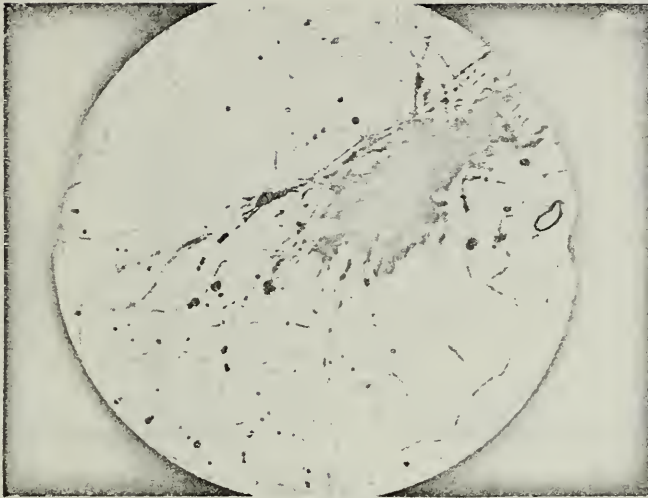


C. 6.2% gross wt. gain
X 500

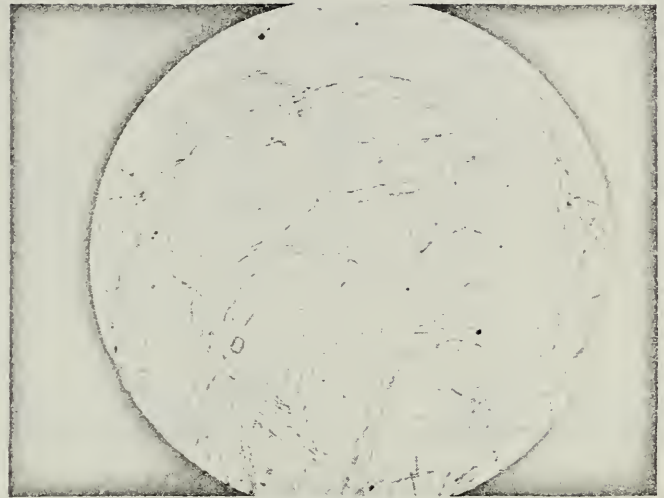


D. 6.2% gross wt. gain
X 500

FIGURE 28. Polyoxymethylene coated cotton fibers: effect of immersion in cupriethylene diamine solvent (Longitudinal view).



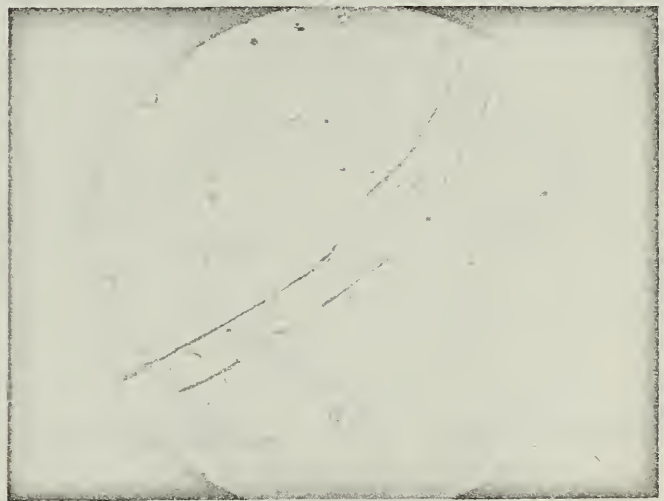
A. 13.1% gross wt. gain
X 125



B. 13.1% gross wt. gain
X 125

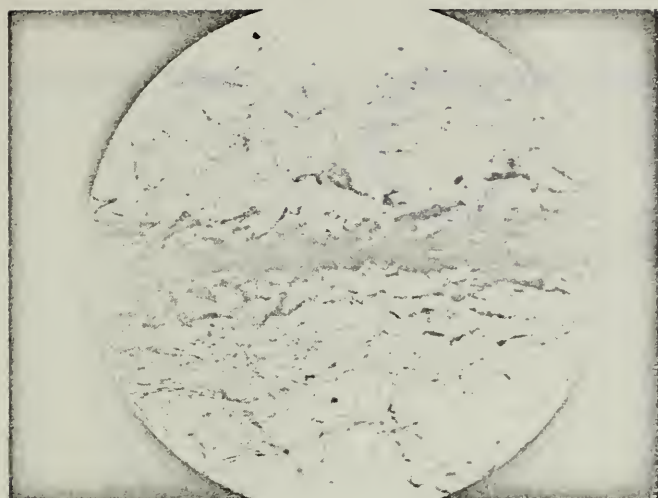


C. 13.1% gross wt. gain
X 500



D. 13.1% gross wt. gain
X 500

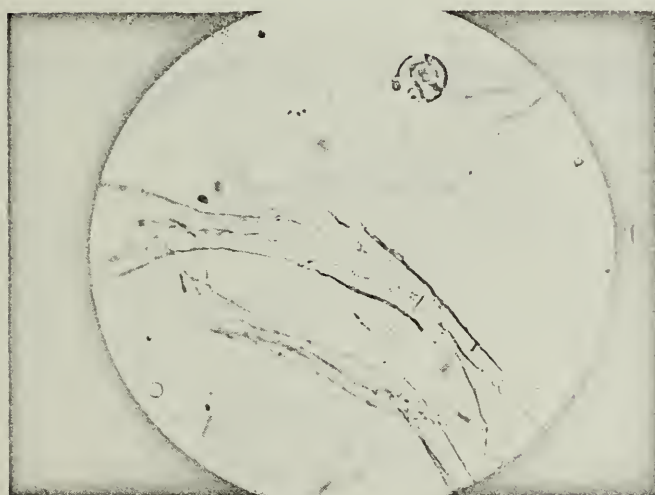
FIGURE 29. Polyoxymethylene coated cotton fibers: effect of immersion in cupriethylene dianine solvent (Longitudinal view).



A. 19.2% gross wt. gain
X 125



B. 19.2% gross wt. gain
X 125

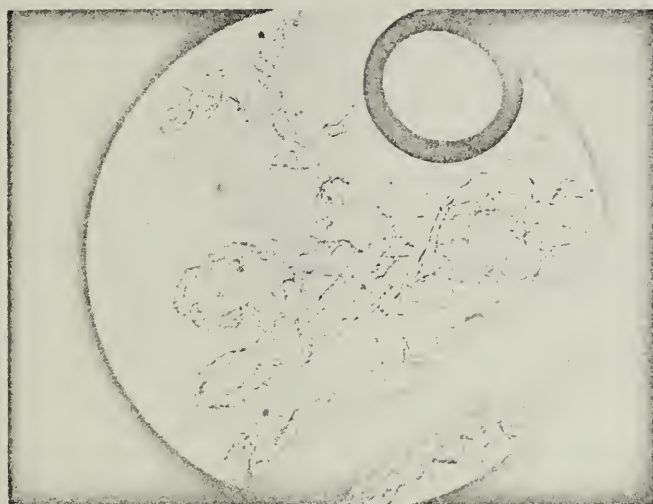


C. 19.2% gross wt. gain
X 500



D. 19.2% gross wt. gain
X 500

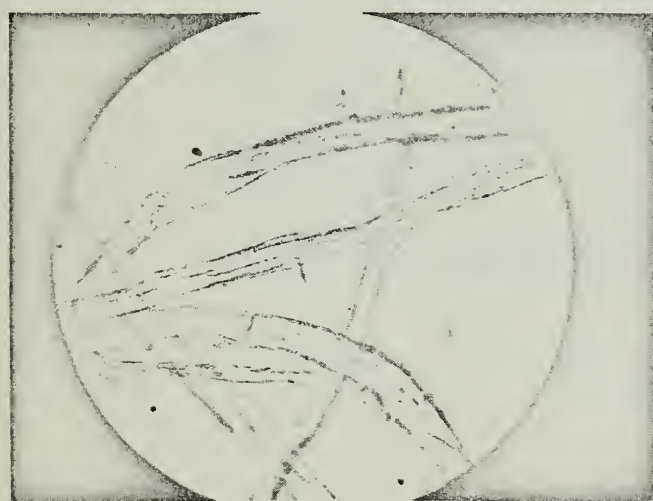
FIGURE 30. Polyoxymethylene coated cotton fibers: effect of immersion in cupriethylene diamine solvent (Longitudinal view).



A. 38.3% gross wt. gain
X 125



B. 38.3% gross wt. gain
X 125

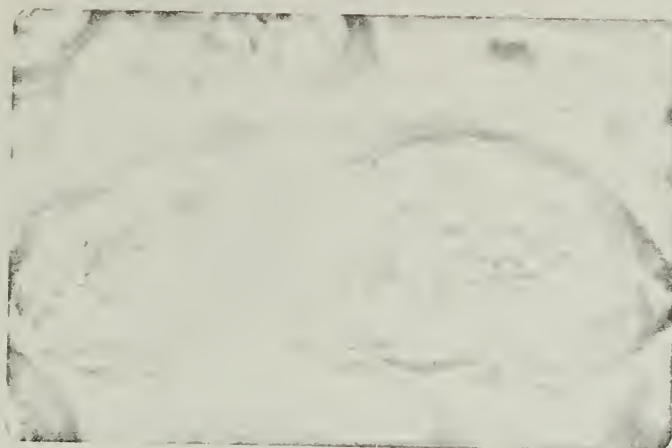


C. 38.3% gross wt. gain
X 500

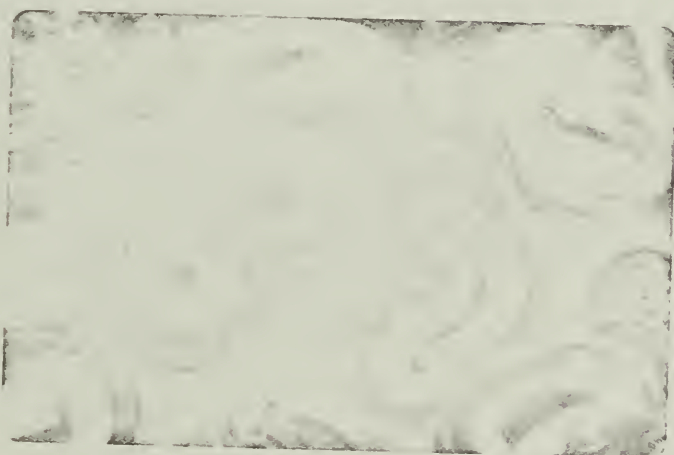


D. 38.3% gross wt. gain
X 500

FIGURE 31. Polyoxymethylene coated cotton fibers: effect of immersion in cupriethylene diamine solvent (Longitudinal view).

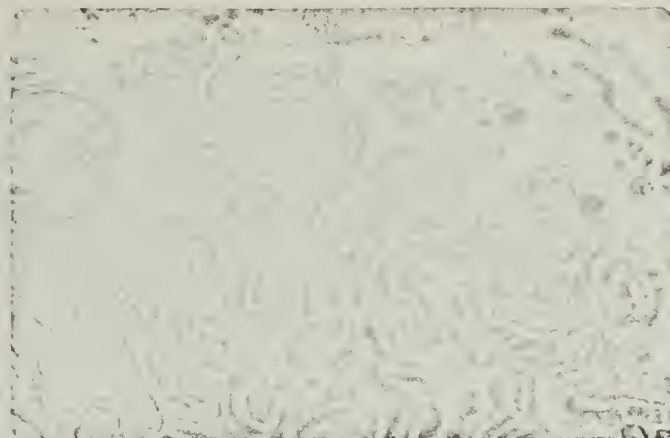


A. X 1250
12% wt. gain



B. X 1250
22% wt. gain

Fig. 32. Cross Sections of Polyoxymethylene Coated Cotton; Polymer Coated with Geigy Dispersion Dye (Setacyl Blue - 2 GS Conc. 250%).



C. X 500
50% wt. gain



D. X 500
50% wt. gain

Fig. 32. Cross Sections of Polyoxymethylene Coated Cotton; Polymer Coated with Geigy Dispersion Dye (Setacyl Blue - 2 GS Conc. 250%).

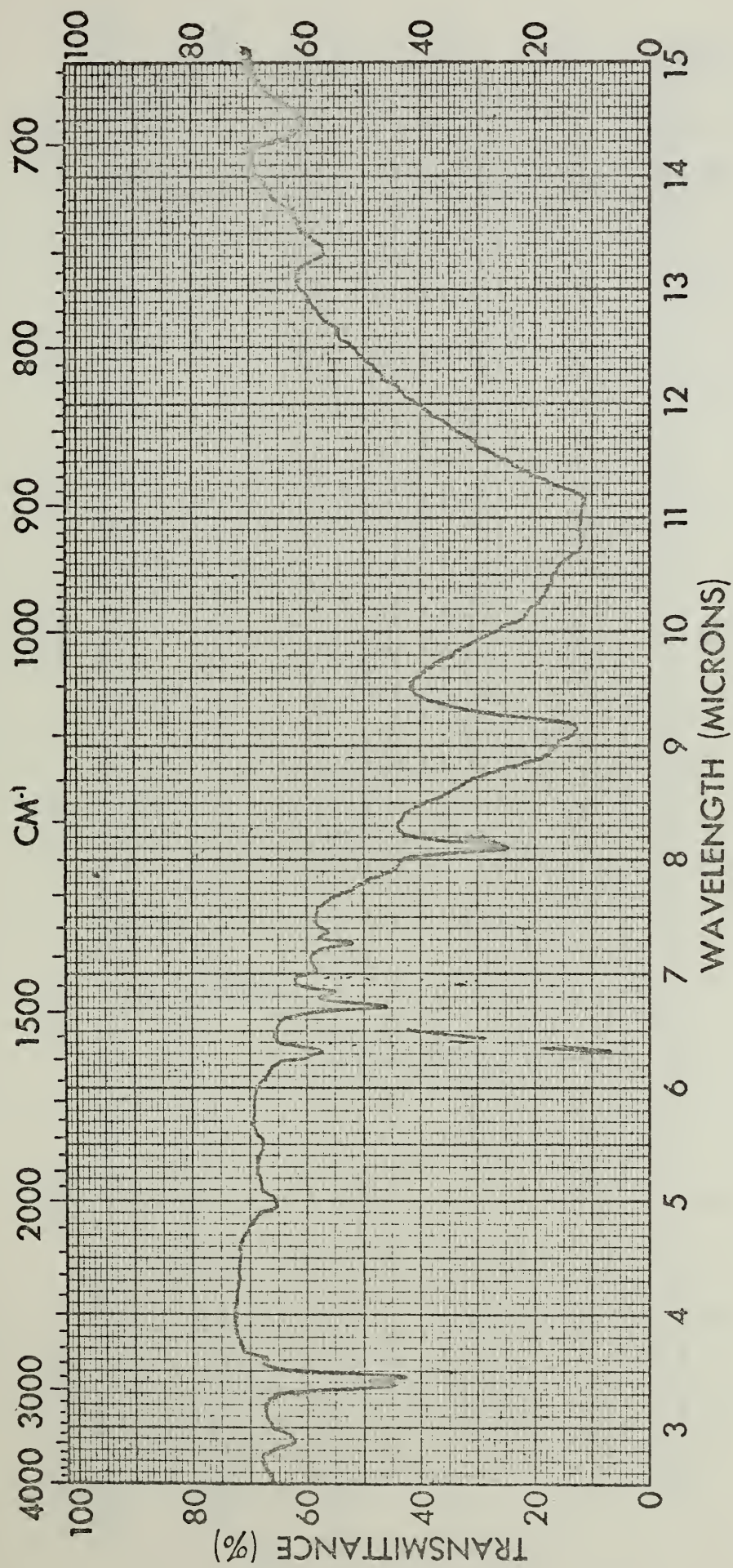


FIG.33. Infrared Spectrum of Polyoxymethylene Film.

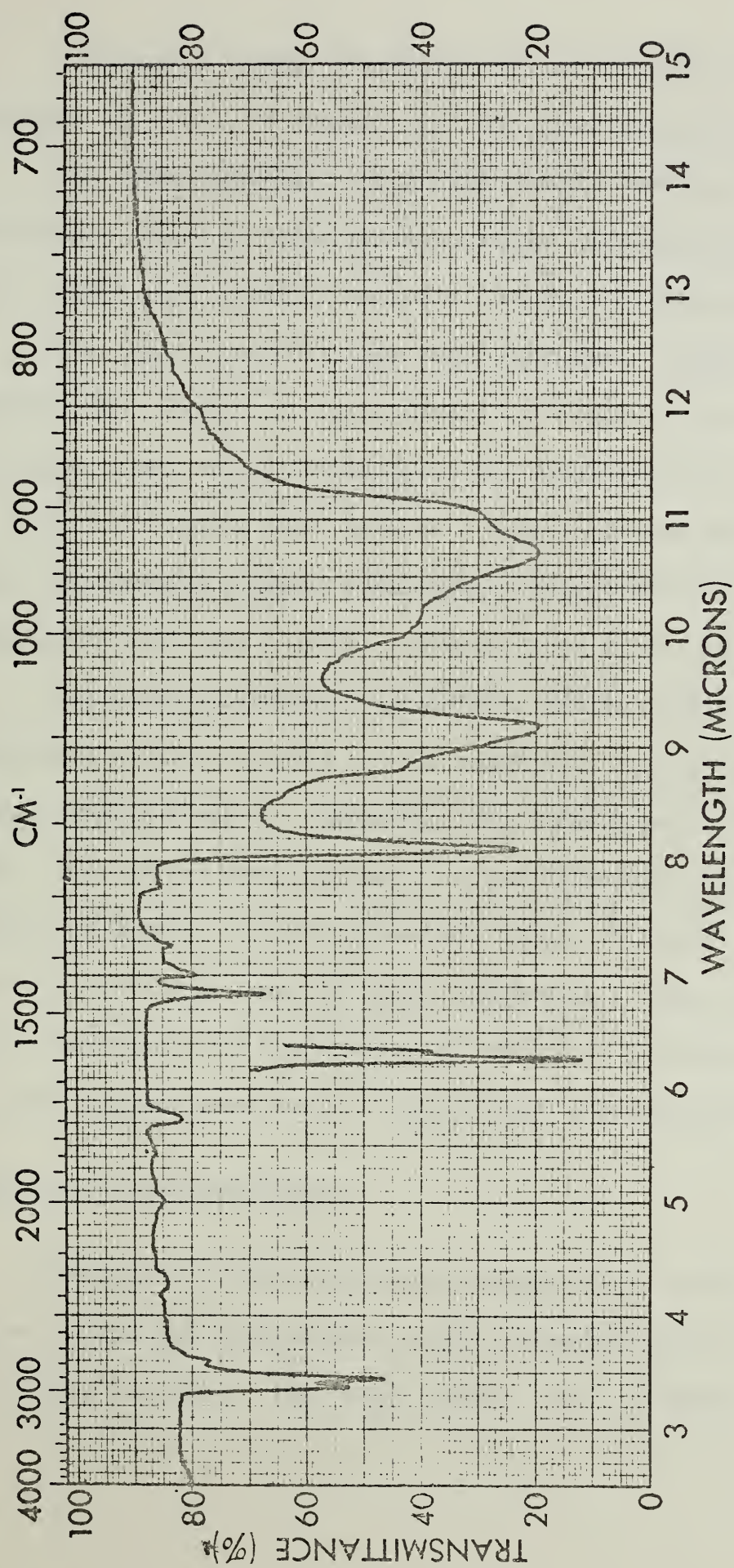


FIG. 34. Infrared Spectrum of "End-Capped" Polyoxymethylene Film.

A review of Tables 10 through 18 and studies of the information deduced from Fig. 27 suggest the following considerations:

All other variables being fixed (e.g., monomer concentration, polymerization reaction temperature, catalyst concentration), the % gross wt. gains indicative of amount of polyoxymethylene deposition increase as the vapor exposure times are lengthened. Except for the first few minutes, the % gross wt. gain versus the vapor exposure time curve is a straight line. Fig. 27 indicates the existence of an "induction" period during the initial few minutes. Such induction period during which the appropriate monomer equilibrium concentration is established, has previously been noted in the polymerization of aldehydes.

The dimethylformamide extraction studies (Table 17) show that the deposited polyoxymethylene can be completely removed from the cloth substrates within 2 hours. Similarly, the "end-capped" polyoxymethylene can, also, be removed when subjected to such dimethylformamide solvent extraction, although a longer extraction period (6 hours) is needed to completely remove them from the cloth substrates. These studies are, therefore, indicative of the absence of cellulose grafting or cross-linking with polyoxymethylene or "end-capped" polyoxymethylene.

Discussion of Photomicrographs:

The black and white photomicrographs shown on Figs. 28-31 are considered to furnish particularly useful information as to the character of the polymer deposits. The fiber samples shown in these photomicrographs

were prepared by exposure of the fiber specimens to cupriethylene diamine for 5 min. and 30 min., followed by photographic examination. As has been mentioned previously, the immersion time of coated cloth in the cellulose solvent is an important factor in determining complete dissolution of cellulose. If the immersion time is not sufficient (e.g., 5 min.) some cellulose remains undissolved, whereas at an immersion time of about 30 min., complete dissolution of cellulose takes place at ambient temperatures.

Fig. 28 A at 125x shows polymer shells or tubes of the sample with 6.2% gross weight gain. The coated cloth sample was treated with cupriethylene diamine solvent for 5 min. As a result, some undissolved cellulose can be seen. In Fig. 28 B no such undissolved cellulose is noted (30 min. immersion time in the cellulose solvent). Figs. 28 C and 28 D at 500x show polymer tubes which are apparently quite uniform and transparent. Figs. 29-31 can be interpreted similarly. It is to be noted that as the % gross wt. gain of cloth sample increases, random clumps or "dendrites" begin to form with increasing frequency and the polymer tubes are no longer smooth as a result of this irregular growth. Similar photomicrographs can be obtained by treating "end-capped" polyoxymethylene coated cloth samples with cupriethylenediamine solvent. They have not been presented here to avoid repetition. The complete solubility of cellulose when coated samples are treated with cupriethylenediamine solvent leaving undissolved polyoxymethylene homopolymers as well as the complete removal of deposited polyoxymethylene from the cloth substrates by dimethylformamide solvent indicate absence of cellulose grafting and/or cross-linking.

Figs. 32 (A,B,C and D) are selected color photomicrographs prepared from 35 mm. slides of stained and cross-sectioned samples of polyoxymethylene coated cloth with % gross wt. gains in the range of 12-50. The blue colored portions indicate the dye stained polymer coatings in these pictures.

Figs. 32-A and 32-B show two fiber cross-sections with the dye stained polymer coatings around the fibers. Figs. 32-C and 32-D show that at high polymer add-on (50%) only the fibers at the outer periphery of the yarn are stained with the dye. The heavy coating prevents the dye from penetrating to the inner core of the yarn, and as a result no staining of the fibers on the inner core can be seen.

A study of certain physical test data presented in Table 18 show that the physical properties such as breaking strength and elongation, tearing strength, and abrasion resistance can be enhanced by the vapor phase encapsulation of cotton cloth samples with polyoxymethylene. The abrasion resistance increases considerably as the wt. gains increase. The % gross wt. gains do not seem to exert too much influence on the breaking and the tearing strengths - nevertheless, these values are improved compared to the control values.

The melting points of polyoxymethylene and "end-capped" polyoxymethylene are the same (165°C). The molecular weight of polyoxymethylene, calculated from the inherent viscosity (0.865), is approximately 11,000-12,000.

Fig. 33 is the infrared spectrum of polyoxymethylene film. The absorption bands at 2.9 microns (characteristic of OH bond), 3.4 microns

(where C-H is known to absorb), and 9.2 and 10.7 microns (where C-O-C bonds absorb), are characteristic of polyoxymethylene. Fig. 34 is the infrared spectrum of "end-capped" polyoxymethylene. The absorption band at 2.9 microns, which is attributed to OH, disappears and is replaced by absorption band at 5.75 microns, which is due to the presence of the C=O groups. These C=O groups are introduced into the "end-capped" polyoxymethylene by esterification of the terminal OH groups of polyoxymethylene with acetic anhydride. The bands on Fig. 34 match with those of Delrin.

Conclusion:

A novel reproducible and effective method for the vapor phase encapsulation of cotton fiber cloth samples with polyoxymethylene has been developed. Information on growth characteristics of polymer, degree of uniformity of polymer coatings can be obtained from a study of the photomicrographs. Typically, the polymer has a melting point of 165°C and a number average molecular weight of approximately 11 - 12,000. In sharp contrast to the acid catalyzed formaldehyde processes conventionally employed, the method developed in this investigation is unique in that it maintains or even increases the basic physical strength properties of cotton fabrics.

Acid catalyzed reactions involving the cross-linking of cotton with formaldehyde or reactive derivatives thereof, increase the wrinkle recovery values. However, due to the employment of acid catalysts and the need for severe reaction temperatures frequently ($> 120^{\circ}\text{C}$), the cotton physical strength properties such as breaking and tear strengths as well as abrasion resistance and elongation are severely decreased.

The base catalyzed process as developed does not involve chemical reaction (cross-linking) with cotton substrate and hence, the resulting product is not expected to show any appreciable gains in the wrinkle recovery. This will be experimentally evaluated. The improved physical strength properties of the encapsulated cottons are attributed to the deposition of high molecular weight polyoxymethylene in conjunction with the use of relatively weak basic catalyst which does not attack the cotton cellulose substrate.

Thermal stabilization of the polyoxymethylene homopolymer hydroxyl end groups, previously described as "end-capping", has been effected by using acetic anhydride, which is monofunctional. The employment of difunctional anhydrides such as maleic anhydride and/or other multifunctional compounds should render it possible to cross-link the cotton as well as to "end-cap" the polyoxymethylene homopolymers. Such multifunctional compounds should increase the wrinkle recovery values hopefully without deteriorating the improved physical strength properties of the polyoxymethylene coated cotton fabrics.

This section of the report is concerned with the further development of the previously described formaldehyde monomer based vapor phase polymerization system with emphasis on cross linking studies of the polyformaldehyde polymer coated cotton fabrics in order to develop wrinkle resistance characteristics, etc. Experiments were also initiated on the liquid phase polymerization of formaldehyde monomer to obtain data relevant for a comparison with vapor phase processes.

Cross linking treatments for polyformaldehyde
coated cotton fabrics.

A primary objective of cross linking finishing treatments for cotton fabrics is to provide them with improved shape-holding properties such as wrinkle resistance, wash wear characteristics and dimensional stability while minimizing the loss of durability of cotton in so-called permanent press garments⁽¹⁸⁾. The reduction in fiber toughness and fixation of the fabric geometry brought about presumably by the cross linking of the cellulose are directly related to the lowered durability of such cross linked cotton fabrics⁽¹⁹⁾. Decreased physical strength properties and greater abrasive wear are considered to be the most significant undesirable fabric property changes resulting from the application of cross linking finishing treatments to cotton fabrics and measurements of these fabric parameters are increasingly employed for evaluation purposes.

Polyoxymethylene coated cotton fabrics have been found to exhibit improved physical strength properties tentatively attributed to the deposition of high molecular weight polymer in conjunction with the use of a relatively weak basic catalyst which does not attack the cotton cellulose substrate. It is the current purpose to describe and discuss experiments directed towards the cross linking of polyformaldehyde encapsulated cotton fabrics in order to develop superior shape holding properties such as are required for permanent press garments. Such investigations are in order because the base catalyzed polyformaldehyde polymerization process as developed does not involve chemical reaction with the cotton substrate and, given the thermoplastic character of the polymer, does not and as a matter of fact would not be expected to show

any significant improvements in wrinkle recovery, dimensional stability and other indicators of improved fabric shape holding ability.

The number of cross linking finishing treatments which have been proposed in the technical literature and experimentally investigated to some extent, is very large indeed. The methylol derivatives of urea and melamine, methylol derivatives of cyclic ureas, methylol carbamates are among the more widely used cross linking finishing agents. Other types of cross linking agents that have been employed to a more limited extent include the diepoxides, beta substituted diethyl sulfones, acetals, and aziridinyll compounds. The choice of a cross linking finishing treatment frequently represents a rather complex compromise between performance and cost applied to a specific product with a given processing equipment capability. For purposes of the preliminary experimental studies which are described below, the following cross linking finishing treatments were investigated experimentally with polyoxymethylene encapsulated cotton fabrics:

- a) modified methylolamides, e.g. Rhonite R-1 (Rohm & Haas Co.)
dimethylolethyleneurea, American Cyanamid Aerotex Reactant LC
unbuffered glyoxal based reactant and American Cyanamid's
Reactant 1, a non-resinous cyclic uron derivative.
- b) multifunctional carboxylic acids, e.g. maleic acid; 1,2,3,4
cyclopentanetetracarboxylic acid, trimellitic acid, mellitic
acid and 1,2,3,4 butanetetracarboxylic acid.
- c) epichlorhydrin and difunctional epoxides obtained from the
Shell Chemical Co.

Depending upon the results obtained it was planned to further investigate these and/or other potential cross linking agents.

Pertinent experimental details are summarized as follows.

The test fabrics employed throughout this part of the study were 80 x 80 desized, bleached, mercerized cotton print cloths. Multiples of 10" x 6" fabric samples were cut from the 80 x 80 print cloths for use in the subsequently described vapor phase polymerization and cross linking studies. All cloth samples were coated with polyoxymethylene via vapor phase polymerization of formaldehyde prior to the cross linking experiments.

The specific polymerization catalyst employed in this investigation was prepared by dissolving 7.5 cc of tri-n-butyl amine (obtained from Eastman Organic Chemicals, Rochester, N.Y.) and 3.6 g. of diphenylamine (obtained from Fisher Scientific Co., New York) in 1500 ml of carbon tetrachloride (reagent grade, also obtained from Fisher). A slurry of paraformaldehyde in paraffin oil was prepared by mixing thoroughly 75 g. of paraformaldehyde (obtained from Fisher Scientific Co.) with 300 ml of paraffin oil in a half liter resin bottle. Formaldehyde monomer was generated by heating this slurry. The monomer was carried to the reaction chamber in dry nitrogen gas.

Preparative details for the conditioning activation and subsequent vapor phase encapsulation of the cotton cloth samples also followed the earlier described procedures except that the end capping treatments were omitted for obvious reasons. Also the tests employed for evaluation of the polymer coated cotton samples were conducted in accordance with the details previously described.

Modified methylol amides

The most widely commercially employed cellulose cross linking agents are undoubtedly the so-called methylol amides⁽²⁰⁾. The cross linking studies therefore emphasized the possible applicability of selected cross linking agents derived from this general class, for improving the shape holding characteristics of polyoxymethylene encapsulated cotton fabrics. Experiments were therefore carried out involving the reaction of polyoxymethylene encapsulated cotton fabrics with cross linking finishing systems based on typical methylol amide cross linking agents, as a function of polyoxymethylene polymer add-on. Other variables which were investigated in this work include the concentration of the cross linking agent, the concentration of the necessary catalyst, the curing temperature and time, etc.

A rather typical simplified cross linking procedure was employed for these experiments. Conditioned test samples of cotton cloth coated with known amounts of polyoxymethylene, were treated with aqueous solutions comprising 5 wt. % of the active cross linking agent, 1% catalyst ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), 2% polyethylene emulsion and 0.1% Triton Wetting agent for approximately 10 minutes at ambient temperatures. The samples were then dried for 15 minutes in an air circulating oven at 80°C. Curing was accomplished by heating the treated samples for predetermined time periods at temperatures selected in the 140-165°C range in a forced draft oven. The samples were then washed, dried to constant weight etc. and subjected to the various evaluation tests traditionally employed for cross linking finishes.

As indicated above three cross linking agents were experimentally investigated namely Rohm & Haas' Rhonite R-1 dimethylol-ethyleneurea, American Cyanamid Aerotex Reactant LC (an unbuffered glyoxal based cellulosic textile reactant) and American Cyanamid Aerotex Reactant 1 described as a non-resinous melamine uron type of cross linking compound. The polyethylene emulsion employed was Mykon SF supplied by the Sun Chemical Corp. (Chemical Div. Wood River Junction, R.I.). The wetting agent was Triton XL05 an alkyl phenoxy polyethoxy ethanol produced by Rohm and Haas, Philadelphia, Pa.

Preliminary experimental data on the properties of some cross linked polyoxymethylene coated cotton fabrics are summarized in both tabular and graphical form below. It need scarcely be emphasized that considering the very large number of possible reaction variables which would all have to be explored to obtain a complete analysis of their interactions and effects with respect to the product properties, these data should be considered as indicative of trends only. They certainly do not represent any attempts at optimization which must await later additional investigations. Given these limitations they do however suggest certain possible realizable improvements as will be discussed below.

It is noteworthy that, as expected, all the cross linked polyoxymethylene coated cotton fabrics proved to be insoluble upon immersion in cuene. Experiments were also carried out to ascertain the thermal stability of these cross linked polyoxymethylene encapsulated cotton cloths. Elevated temperature tests conducted in accordance with previously described procedures demonstrated a degree of thermal stability which is indicative of cross linking with end capping.

Tables 17 and 18 summarize some of the basic physical strength properties of polyoxymethylene coated cotton fabrics treated with two of these cross linking finishing systems, namely Rhonite R1 and Aerotex Reactant LC. Data on the treatment with Aerotex Reactant 1 appear similar to Aerotex Reactant LC and have not been detailed. Percent strength retention of the Rhonite R1 and the Aerotex LC cross linking agent treated polyoxymethylene coated cotton fabrics have been plotted as a function of total add-on in Figures 35 and 36. These figures also compare the strength retention of the cross linked polyoxymethylene coated cotton fabrics with those of cotton fabrics treated only with the cross linking finishing agent (i.e. cross linked, uncoated cotton cloth samples).

Because of some loss of the uncapped polyformaldehyde during the high temperature curing step with these modified methylool amide type cross linking agents, the accurate quantitative determination of the amount of cross linking agent add-on presents somewhat of a problem. The weight gains shown are based on comparisons with unmodified, i.e. uncoated cotton cloth samples treated simultaneously with the same cross linking agent system. The amount of cross linking agent deposited on the polymer coated cotton cloths was in the order of 1.3 - 3.0 % based upon the weight of the untreated cloths. Analytical studies with emphasis on cross linked polymer coated samples with low total weight gains - 5% or less - are continuing as this range of add-ons appear to offer a potentially most interesting balance of properties.

Table 17. Some physical properties of polyoxymethylene coated cotton cloths treated with Rhonite R-1 cross linking agent

Group A Samples					
Sample	% Add-on ¹⁾	Breaking Strength ²⁾ (lbs.)	% Elongation ²⁾	DMR ³⁾ (W + F)	WFW ⁴⁾ (W + F)
Control	-	43.5	21.5	195	185
C-A ⁵⁾ 1	1.5	24.0	22.0	272	-
C-A 2	3.2	19.8	21.9	296	279
C-A 3	3.6	18.7	19.9	317	-
C-A 4	1.5	29.0	24.1	284	268
C-A 5	2.1	23.0	19.3	302	-
231	3.7	38.3	23.2	224	240
232	6.8	39.3	23.5	271	259
265	3.0	26.7	23.2	302	285
270	13.3	35.5	23.9	248	237
271	10.0	28.8	22.3	-	-
272	9.6	28.8	20.0	-	-
225	16.0	35.8	19.0	-	-
235	18.7	37.2	17.7	196	180
236	18.3	33.8	18.2	200	175
237	22.1	38.5	19.3	-	-
238	25.4	48.0	22.9	153	140
227	27.0	48.0	23.0	-	-
310	26.2	32.8	16.4	-	-
297	33.6	36.2	17.2	151	138
320	36.8	38.8	15.8	-	-

- 1) Percent add-on represents the total weight gain due to the polyoxymethylene and the cross linking agent after cure except those samples designated C-A, etc. (See footnote 5).
- 2) ASTM D1682-64; Average of three runs per sample, fill direction only.
- 3) ASTM D1295-60-T; Average of three runs per sample.
- 4) ASTM D1295-60-T; Average of three runs per sample; samples conditioned for five minutes in 0.1% Triton X-100 solution.
- 5) Control samples treated with cross linking agent only.

Table 18. Some physical properties of polyoxymethylene coated cotton cloths treated with Aerotex React LC cross linking agent

Group B Samples					
Sample	% Add-on ⁽¹⁾	Breaking Strength ⁽²⁾ (lbs.)	Elongation ⁽²⁾	DRW ⁽³⁾ (W + F)	WRW ⁽⁴⁾ (W + F)
Control	-	43.5	21.5	195	185
C-B ⁵ 1	2.9	27.2	23.2	298	-
C-B 2	1.7	30.7	24.9	249	234
C-B 3	1.5	30.5	27.0	246	-
C-B 4	1.8	27.2	22.7	254	242
C-B 5	2.3	24.2	21.4	300	290
326	3.3	41.2	25.6	232	245
327	2.7	40.2	27.5	217	230
328	3.7	43.7	27.1	205	195
313	6.5	31.5	20.0	-	-
325	6.8	32.3	22.4	-	-
244	8.7	30.0	19.1	-	-
303	9.5	44.3	27.7	187	-
329	12.5	32.5	19.8	-	-
323	15.9	27.3	18.3	195	178
240	17.3	30.8	16.5	-	-
322	18.1	25.3	16.2	-	-
302	22.3	36.2	19.9	240	210
299	23.1	31.0	16.3	-	-
324	25.4	30.7	18.0	-	-
300	33.4	35.7	14.9	175	162

(1) Percent add-on represents the total weight gain due to the polyoxymethylene and the cross linking agent after cure except those samples designated C-A, etc. (See footnote 5).

(2) ASTM D1682-64; Average of three runs per sample, fill direction only.

(3) ASTM D1295-60-T; Average of three runs per sample.

(4) ASTM D1295-60-T; Average of three runs per sample; samples conditioned for five minutes in 0.1% Triton X-100 solution.

(5) Control samples treated with cross linking agent only.

FIGURE 35. PER CENT STRENGTH RETENTION
VS. TOTAL PER CENT Add-ON^{1,2}

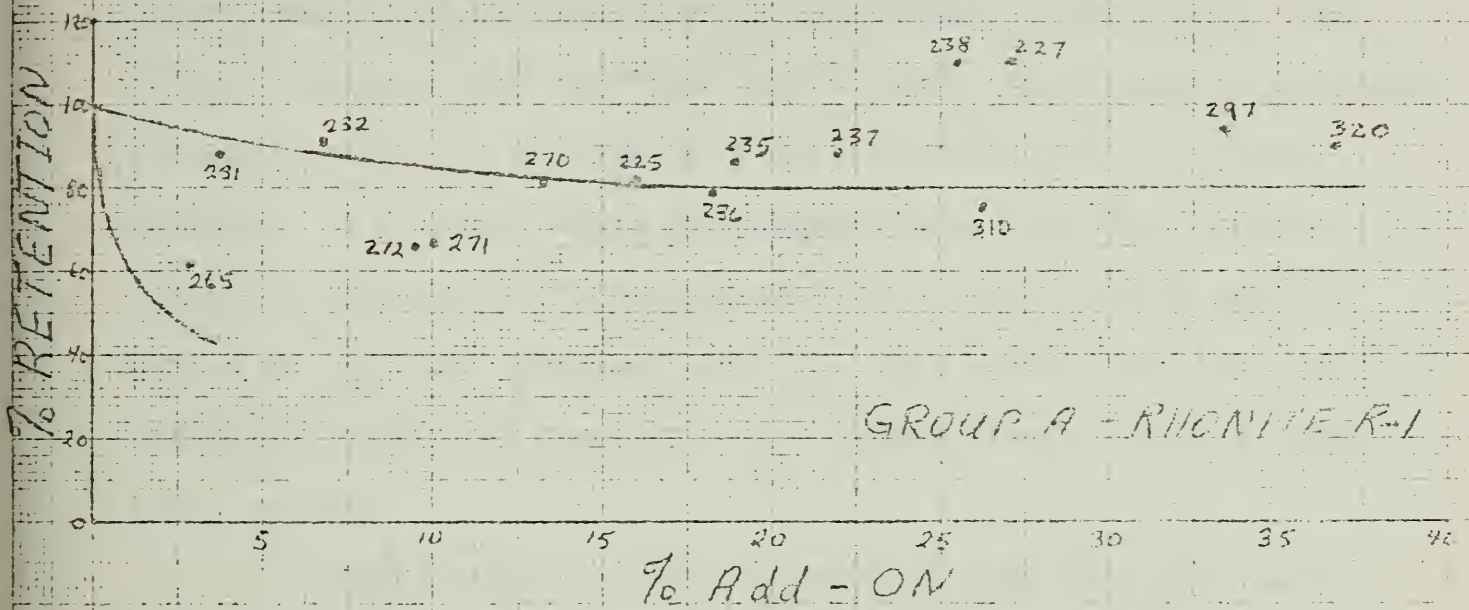
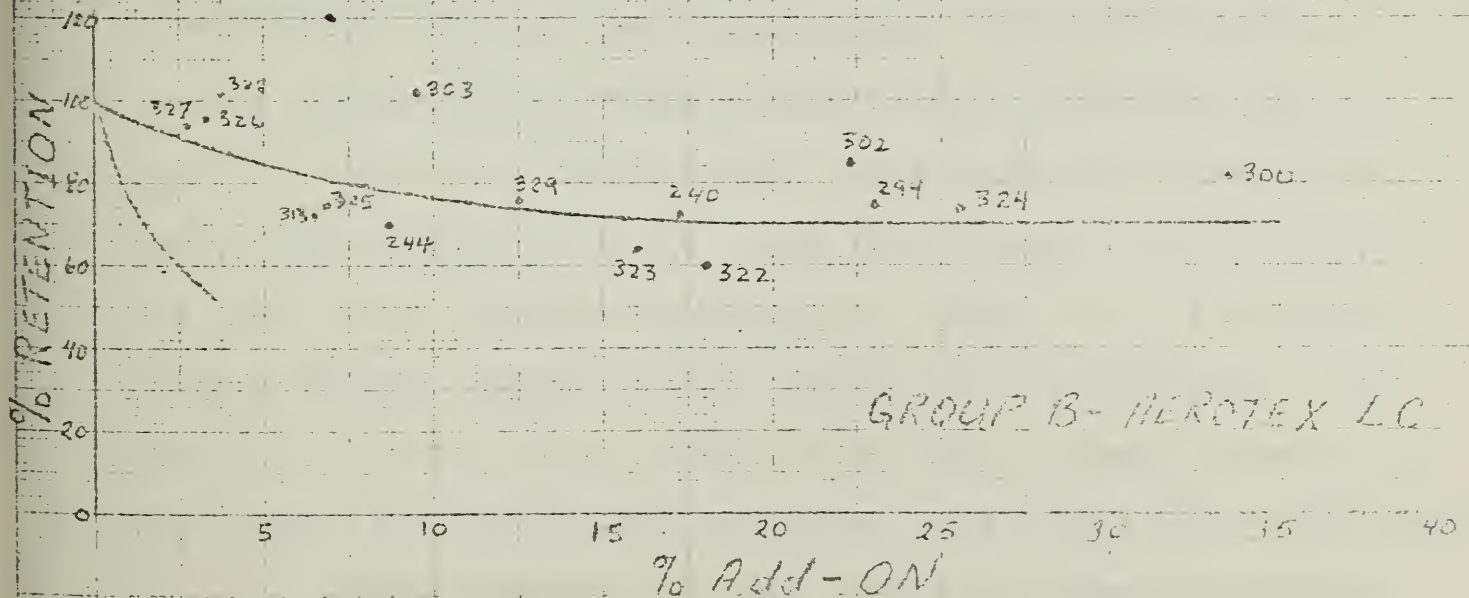


FIGURE 36.



¹ ALL PTS. REPRESENT AN AVERAGE OF THREE RUNS PER SAMPLE - EACH
² PT. LABELLED WITH A SAMPLE NUMBER
 LOWER CURVES REPRESENT STRENGTH RETENTIONS FOR CONTROL
 SAMPLES TREATED WITH CROSS LINKING AGENTS

Experiments have also been carried out and are continuing on the measurement of the abrasion resistance of both the cross linked polymer coated and the merely cross linked cotton cloth samples. Preliminary screening with the Stoll Flex Abrasion tester apparently suggests the superior abrasion resistance of the cross linked polymer coated specimens. A 7% total add-on for example gave a Stoll Flex Abrasion rating of approximately 200 as against 95 for control cotton samples. Because of the known deficiencies of this test method these data are not reproduced pending the completion of a program of cuff abrasion testing now in progress.

Consideration of these experimental data indicates clearly that strength retention approximately in the order of 80%^{*} can be obtained with cross linked cotton samples which had previously been coated with polyoxymethylene from the vapor phase. The shape holding characteristics of these cross linked polymer coated cotton cloths as shown by both dry and wet wrinkle recovery values, is substantially enhanced for Rhonite R-1 treated polymer coated samples in the lower total add-on range, possibly up to 10%. Stoll Flex abrasion resistance measurements also showed significant improvements. Sample No. 232 for example showed a strength retention of 91%, DRW(W+F) of 271 and WWR(W+F) of 259 with 6.8 wt. % total add-on. Sample No. 270 gave a strength retention of approximately 81%, DRW(W+F) 248 and WWR(W+F) of 237 for a 13.3% total add-on.

Aerotex reactant LC did not result in the same improvements in wrinkle recovery as did treatment of the polyoxymethylene coated cotton cloths with the Rhonite R-1 cross linking agents. The reasons for

* Based upon the weight of the original cotton controls.

this are not clear and underscore the need for additional experimental investigations with this and other cross linking agents in order to clarify the various reactions which can occur with these complex finishing systems.

The data also show that cross linking of cotton cloths coated with relatively large amounts of polyoxymethylene (> 20-25%) does apparently not enhance wrinkle recovery. This may be related to the physical presence and inherent characteristics of the polymer. These results again show the need for more experimental data in order to explore the chemical reactions involved when polyoxymethylene coated cotton cloths are reacted with these cross linking finishing agents. Of particular interest is a better understanding of the relative reactivities of the cotton and polyformaldehyde hydroxyls with the cross linking agents and their possible interactions.

Polyfunctional carboxylic acids

The cross linking of cotton cellulose with di- or polycarboxylic acids has been reported by a number of investigators^(21,22) including a recent summary by Campbell and Francis⁽²³⁾ and processes featuring the introduction of ester cross links into cotton by a rapid curing process as described by S.P. Rowland and associates^(24,25). The cross linking via ester formation is of particular interest for the polyoxymethylene coated cotton fabrics because esterification with acetic anhydride has been employed for end capping the polyoxymethylene polymer deposits thus enhancing that polymer's thermal stability. Polyfunctional carboxylic acids may therefore be expected to generate both end capping and cross linking reactions.

A number of polycarboxylic acids were experimentally investigated including the following compounds: maleic acid; 1,2,3,4 cyclopentanetetracarboxylic acid; trimellitic acid, mellitic acid and 1,2,3,4 butanetetracarboxylic acid. These compounds were obtained from the sources listed: maleic acid, Allied Chemical Co.; 1,2,3,4 cyclopentanetetracarboxylic acid, Copolymer Rubber and Chemical Co.; trimellitic acid, Amoco Chemical Co.; mellitic acid, Aldrich Co. and 1,2,3,4 butanetetracarboxylic acid, K & K Laboratories, Inc.

The procedure employed for reaction with these polycarboxylic acids involved the treatment of polyoxymethylene coated cotton fabrics by immersion in two aqueous solutions followed by heating. The first solution comprised 15 wt. % sodium acetate and 0.1 wt. % Triton X 100 wetting agent. The second solution contained 2 wt. % of the polycarboxylic acid. The cotton test samples were dipped in the first solution for approximately 10 minutes in order to promote swelling of the cotton and facilitate the penetration of the catalyst. After removal of excess solution the samples were immersed in the solution of the polycarboxylic acid up to 10 minutes, dried at 80°C for approximately 10 minutes and cured at selected temperatures ranging from 140°-160°C for 15-20 minutes in an air circulating oven. The samples were then washed, dried to constant weight etc. and subjected to the customary fabric evaluation tests.

The precise determination of the polycarboxylic acid "add-on" again presented somewhat of a problem because some loss of the uncapped polyformaldehyde occurs during the high temperature esterification reactions. It was therefore decided to roughly estimate the add-on by comparison with control samples not containing polymer of the same cotton

cloth likewise processed in the manner described above. This is admittedly a far from completely satisfactory procedure because of the altered number and changed accessibility of the hydroxyl groups due to polymer encapsulation. If this is done however the add-ons for the maleic anhydride system in the controls averaged at 1% while the 1,2,3,4 cyclopentanetetracarboxylic acid add-on measured in the order of 1.5-2.0%.

Tables 19 and 20 furnish some basic strength and wrinkle recovery data on two typical polycarboxylic acid reacted polyoxymethylene coated cotton cloth samples, namely maleic and 1,2,3,4 cyclopentanetetracarboxylic acid. All the samples treated with these reagents were investigated for cross linking by immersion in 0.5 M cuene and found to swell but not dissolve after a one hour soaking period. Swelling was accentuated by moderate temperature increases but again solution did not occur.

Experiments were also conducted on selected samples to evaluate thermal stability. This was done by exposure of the polycarboxylic acid treated polyoxymethylene coated samples to temperatures of 150-160°C for a minimum 20 hour period and comparing the results with similar exposure tests carried out with cotton cloths coated with polyformaldehyde but not end capped. The thermal degradation rates of the maleic acid and the 1,2,3,4 cyclopentanetetracarboxylic acid reacted polymer coated cloths were 0.0002% per min. and 0.00017% per min. compared to 0.1% per min. for the unend capped sample. This indicates that sufficient effective end capping had occurred to assure what is considered to be an adequate degree of composite thermal stability.

Table 19. Some physical properties of polyoxymethylene coated cotton cloths treated with maleic acid.

Sample	% Add-on ¹⁾	Cure Temperature ²⁾	Breaking Strength ³⁾ (lbs.)	DMR ⁴⁾ (W + F)
Control	-	-	53	166
Group A				
53	5.4	160	30	190
55	4.3	160	23	200
56	6.0	160	27	200
57	4.3	160	25	210
59	7.7	160	44	190
76	4.6	140	38	158
85	6.2	140	43	142
86	6.6	140	56	86
Group B				
61	9.3	160	31	182
72	12.9	160	32	92
79	10.6	160	45	94
81	12.2	140	68	96
82	12.1	140	55	94
83	9.3	140	46	100
87	8.8	140	59	100
Group C				
69	24.3	160	47	56
78	15.2	140	51	100

- 1) Percent add-on represents the total weight gain due to the polyoxymethylene and the cross linking agent after curing.
- 2) All samples cured at the given temperature for 15 minutes in a forced draft oven.
- 3) ASTM-D1682-64; Average of three runs per sample, warp direction only.
- 4) ASTM-D1295-60-T; Average of five runs per sample.

Table 20. Some physical properties of polyoxymethylene coated cotton cloths treated with 1,2,3,4-cyclopentane tetracarboxylic acid. (4)

Sample	% Add-on (1)	Breaking Strength (2) (lbs)	Elongation (2)	DWR (3) (W + F)
Control	-	53	5.8	175
Group A				
140	8.9	35	5.0	-
141	9.3	-	-	185
143	9.6	29	5.4	-
110	7.5	-	-	199
115	7.2	43	6.0	-
120	7.2	42	5.4	-
122	6.8	-	-	188
Group B				
111	5.5	36	5.4	-
112	5.5	-	-	217
113	5.6	35	5.5	-
114	7.5	-	-	196
116	4.8	32	5.8	-
119	6.2	43	6.0	-
121	4.3	-	-	212
124	6.0	38	5.7	-
125	4.1	43	5.8	-
149	3.9	41	5.6	-
Group C				
118	3.3	39	5.6	-
126	3.1	32	5.1	-
127	2.4	36	5.7	-
128	2.6	32	5.8	-
129	3.6	-	-	230
133	1.9	-	-	229
145	2.9	39	5.5	-
146	2.5	-	-	221
147	3.2	30	5.8	-
148	2.8	36	5.9	-

- (1) Percent add-on represents the total weight gain due to the polyoxymethylene and the cross linking agent after curing.
- (2) ASTM-D1682-64; Average of three runs per sample, warp direction only.
- (3) ASTM-D1295-60-T; Average of five runs per sample.
- (4) All samples dipped in 2% acid bath for 10 minutes, dried at 80°C, then cured for 20 minutes at 150°C.

Consideration of the data presented in Tables 19 and 20 indicates that the reaction with these polycarboxylic acids proved not effective in enhancing the shape holding properties of the polyoxymethylene coated cotton fabrics. Furthermore, the amount of the polyoxymethylene deposited onto the cotton fibers did apparently not influence these results, at least up to 25 wt. % loadings. While the strength properties are maintained or even exceeded at the high polymer loadings, wrinkle recovery values were found to be well below those measured for the controls. As shown in Table 19 small polymer loadings give somewhat better wrinkle recovery values with strength retentions in the order of 65%. Because of these rather unsatisfactory results, abrasion resistance testing was omitted for this test series.

Epichlorhydrin and diepoxides

Epichlorhydrin as well as various other epoxy compounds have long been proposed as cotton reactants and have been experimentally investigated in some detail^(26,27,28). The reactions can be greatly modified by various salts in the presence of alkaline catalysts. An improved balance of wrinkle recovery properties has been reported for epichlorhydrin by pretreatment with concentrated solutions of sodium orthosilicate, sodium metasilicate or trisodium phosphate at 80°C.⁽²⁶⁾ The treatment of cotton with the reaction products of epichlorhydrin and ammonia has also been studied⁽²⁷⁾. It was deemed of interest to explore the reaction of epichlorhydrin and certain other epoxy type compounds with unendcapped polyoxymethylene coated cotton fabrics in order to achieve both thermal stabilization and cross linking as evidenced by enhanced shape holding properties, solubility studies, etc.

Polyoxymethylene coated cotton fabrics were reacted with epichlorhydrin in the presence of an alkaline catalyst using a two dip procedure. Reaction conditions were arranged in such a manner that the polyoxymethylene polymer add-ons amounted to between 8 and 12%, based upon the initial weight of the conditioned cotton cloths. In the first process step the samples were immersed in a 5 wt. % sodium hydroxide solution in absolute ethanol. After removal of excess solution, the swollen samples were exposed to a 20% by volume epichlorhydrin solution in absolute ethanol. Curing was accomplished in an air circulating oven at 100°C for 10 minutes. The products were found to be insoluble in cuene.

Preliminary data are summarized in Table 21. It will be noted that only very low weight gains were obtained even though initial polyformaldehyde loadings of the cotton were quite substantial in certain cases. This indicates that the epichlorhydrin reaction degraded the polyoxymethylene under the specific experimental conditions employed. This treatment is therefore not suitable for the proposed aims of these experiments. Based on the wrinkle recovery and strength retentions measured, the amount of cross linking which had occurred, must have been limited. It is speculated that the main reaction occurred between the polyformaldehyde and the epichlorhydrin.

Liquid phase polymerization of formaldehyde monomer onto the surfaces of cotton fibers

Experiments were initiated on the liquid phase polymerization of formaldehyde monomer onto the surfaces of cotton fibers for comparison purposes, with the previously described vapor phase polymerization processes.

Table 21. Some physical properties of polyoxymethylene coated cotton cloths treated with epichlorohydrin. (6)

Sample	% Add-on ¹⁾	Breaking Strength ²⁾ (lbs.)	% Elongation ²⁾	(W + F) DWR ³⁾	(W + F) WWR ⁴⁾	Elmendorf Tear ⁵⁾ (Gms)
Control	-	53	5.8	166	150	470
130	1.7	-	-	-	-	459
131	1.8	-	-	214	210	-
132	2.6	43.3	9.3	-	-	-
134	2.4	-	-	-	-	491
117	1.2	35.9	7.8	-	-	-
155	.26	-	-	172	208	-
156	3.4	43.6	8.8	-	-	-
157	.50	-	-	-	-	517
158	.90	-	-	190	200	-
159	.80	44.3	8.5	-	-	-
164	1.8	-	-	-	-	517
165	.33	-	-	182	170	-
166	.30	37.3	8.4	-	-	-
167	.12	-	-	-	-	512
168	.29	-	-	178	174	-
169	.60	41.6	8.4	-	-	-
170	1.8	41.3	9.1	-	-	-
171	.98	-	-	-	-	501
172	.60	-	-	202	218	-
173	2.0	41.8	8.8	-	-	-
174	1.5	-	-	-	-	560
175	2.0	-	-	192	212	-
176	1.0	45.8	9.7	-	-	-
177	1.8	-	-	-	-	533
178	1.7	-	-	166	156	-
179	1.2	42.8	8.8	-	-	-
180	.87	42.0	8.7	-	-	-
181	.35	-	-	-	-	512
183	.85	-	-	212	184	-
184	1.0	40.9	8.0	-	-	-
185	2.5	-	-	-	-	491
186	2.0	-	-	192	194	-
187	3.1	40.8	8.4	-	-	-
188	2.3	-	-	-	-	528
189	1.9	-	-	192	198	-

- 1) Percent add-on represents the final weight gain resulting after curing.
- 2) ASTM-D1682-64; Average of 4 runs per sample, warp direction only.
- 3) ASTM-D1295-60-T; Average of 5 runs per sample
- 4) ASTM-D1295-60-T; Average of 5 runs per sample; samples conditioned for five minutes in 0.1% Triton X-100 solution.
- 5) ASTM-1424-63; Average of 3 runs per sample, warp direction only.
- 6) All samples dipped in 5% NaOH, then 20% epichlorohydrin (both in absolute ethanol), then cured for 10 minutes at 100°C in a forced draft oven.

The chosen experimental procedure can best be described as a liquid phase modification of the hitherto employed vapor phase polymerization technology, purified dry formaldehyde monomer gas being bubbled into an organic liquid phase containing activated cotton cloth test samples. Pyrex glass equipment was employed for the system which proved rather simple to construct. Reaction temperature, time, etc. were controlled in order to obtain reproducible data.

The catalyst system employed for the activation of the cotton cloths was the same as the one employed for the vapor phase polymerization studies, e.g. the tributylamine-diphenylamine mixture in the halogenated solvent previously described. A considerable variety of solvent media were experimented with in order to optimize conditions for both polymerization and polymer deposition. Polymerization proceeds quite readily at ambient temperatures in various organic media. The major problem encountered to date has been to develop enough selectivity to restrict the attempted liquid phase polymerization to the surfaces of the cotton fibers. This is clearly shown in the attached microphotographs of dyed cross sections (Fig. 37) and longitudinal sections (Fig. 38) of cotton fibers subjected to such liquid phase polymerization reactions. The polyoxymethylene polymer deposits were quite non-uniform and represented a series of discontinuous clumps rather than the previously observed much more uniform and continuous tubes of the vapor phase process.

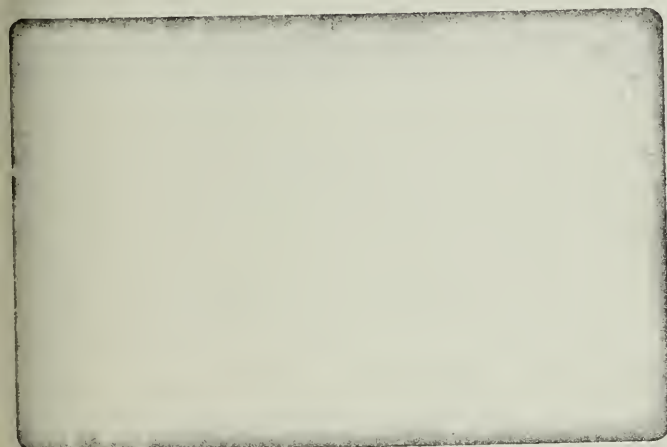
Additional liquid phase polymerization studies are now being conducted with emphasis on the establishment of reaction conditions which will make possible a more selective polymerization restricted to the cotton fiber surfaces. A complete report of these investigations will be



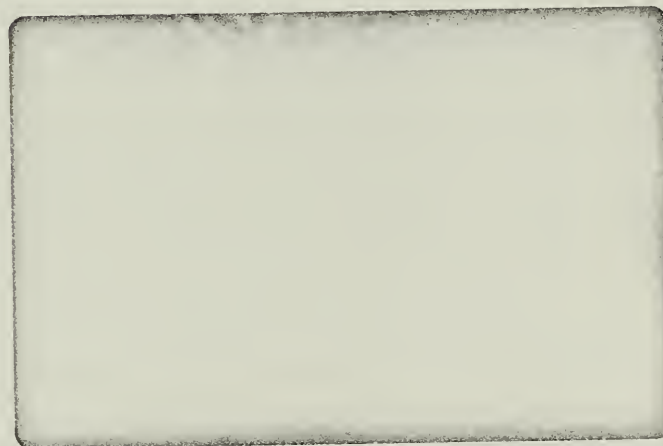
A. X500



B. X500

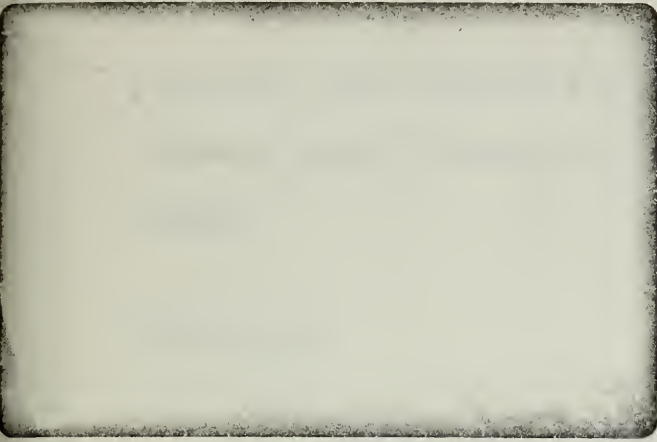


C. X1250

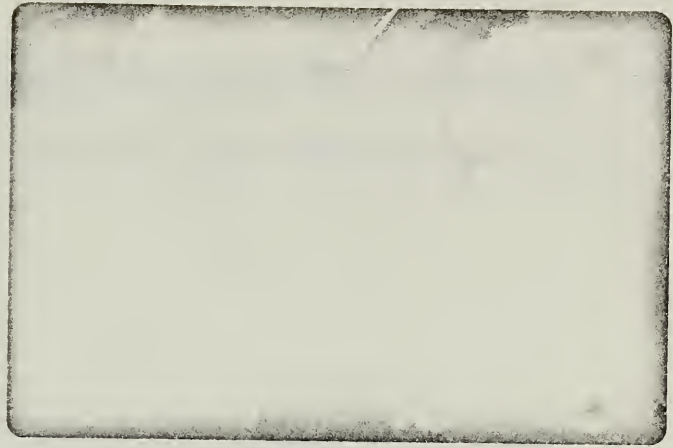


D. X1250

FIGURE 37. Cross Sections of Liquid Phase Polyoxymethylene Coated Cotton; Polymer Dyed with Geigy Dispersion Dye (Setacyl Blue - 2GS Conc. 250%).



A. X500



B. X500



C. X7250



D. X1250

FIGURE 38. Longitudinal Sections of Liquid Phase Polyoxymethylene Coated Cotton; Polymer Dyed With Geigy Dispersion Dye (Setacyl Blue - 2GS Conc. 250%).

presented upon completion of the experimental work now in progress. One approach being followed involves a built in amine catalyst site in the cotton.

Conclusions

Vapor phase polyoxymethylene coated cotton fabrics were treated with various cellulose cross linking agents in order to enhance their shape holding characteristics while maintaining other desirable properties with emphasis on strength retention. One typical cross linking agent dimethylolethyleneurea resulted in strength retentions in the order of 80% and substantially enhanced wrinkle recoveries with relatively small polyoxymethylene loadings and 1.5-3.0% cross linking agent add-on's. Preliminary abrasion data are also promising. Further experiments with this and other modified methylol amide cross linking agents are indicated in order to optimize this approach which is considered to offer considerable promise for obtaining an enhanced balance of cotton properties.

Reactions of polyoxymethylene coated cotton fabrics with selected polycarboxylic acids and epichlorhydrin were also carried out but the results obtained were not promising. Experiments were also commenced on the liquid phase polymerization of formaldehyde onto the surfaces of cotton fibers in order to compare this process with the previously described vapor phase process. The main problem in the liquid phase process was restriction of the polymerization of the formaldehyde monomer only to the cotton fiber surfaces. The possibility of achieving improved selectivity with built in catalyst sites in the cotton is being investigated.

The mechanism of the reaction of methylamide cross linking agents with polyoxymethylene coated cotton cloths is not well understood, and the polyformaldehyde hydroxyl end groups and their possible interactions with these cross linking agents.

C. Polyamide polymer coating modified cotton
fabrics - Interfacial Polymerization

Interfacial polymerization techniques for the preparation of polyamides, polyurethanes and various other condensation polymers have been extensively studied.⁽²⁹⁾ This method of polymer preparation offers several potentially most attractive features for applications such as the modification of textiles with in situ formed condensation polymers. In contrast to slow high temperature polycondensation reactions, interfacial polymerization reactions can proceed at high rates and are capable of giving essentially quantitative yields at ambient temperatures. Furthermore all of the well known types of condensation polymers can be prepared by such low temperature condensation processes, "although specific polymers and subgroups may present exceptions to this conclusion".⁽²⁹⁾ Also thermally unstable intermediates may be employed and thermally stable infusible polymer structures can be synthesized to produce new polymeric structures which otherwise cannot be readily obtained. Direct polymerization to coatings, fibrous particles, fibers and films has been experimentally demonstrated.

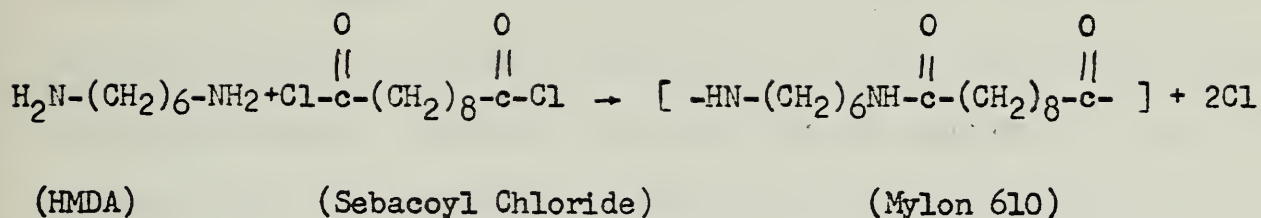
The chemistry of interfacial polymerizations is rather simple. The best known and most widely used of these reactions is that of an organic acid halide with a compound containing an active hydrogen in the functional group such as an amine, phenol or thiol etc. Condensation polymers are formed if the complementary compounds are bifunctional such as a diacid chloride and a diamine. The absolute reaction rates of unhindered aliphatic acid chlorides with primary diamines are "immeasurably fast",⁽²⁹⁾ rates of reactions having been ascertained to be of the order of 10^2 - 10^6 l/mole-sec. in homogeneous solutions - as fast as the propagation step of the fast vinyl polymerizations.⁽³⁰⁾ The principal requirements are that the polymerization rate be appreciably faster than all side reactions and that the polymer should be in solution or "mobile" for a sufficient period of time to attain a high degree of polymerization.⁽³¹⁾ The variables affecting interfacial polycondensation have been described and are relatively easily controllable. Other advantages of this low temperature polymerization method relate to simplicity of equipment and adaptability to commercial production.

If complementary phases for an interfacial polymerization are brought together without stirring and if the organic liquid is a non-solvent for the polymer, a thin film of polymer will be formed at once at the interface. Under the right conditions this polymer precipitate is coherent and tough and has high molecular weight. Liquid phase interfacial polymerization has been extensively studied by Whitfield, Miller and Wasky etc. to shrinkproof wool by the in situ formation of thin coatings of polyamides, polyurethanes and other condensation polymers on wool fibers.⁽³¹⁻³⁶⁾ The procedure employed was to treat the fabric first with a solution of one

reactant and then the other. This general approach appeared of interest for the polymer modification of cotton fibers at low temperatures under experimental conditions which would not deleteriously affect their pertinent desirable performance characteristics.

In view of the results obtained from cross linked polyformaldehyde coated cotton studies it was deemed of interest to ascertain the effects if any of cross linked polyamide coated cotton fabrics on the development of wrinkle recovery properties and other appropriate cotton performance parameters. Experimental studies directed towards these objectives are summarized below using two different types of cross linking agents namely methylolamides and aliphatic diisocyanates.

Polyamides as a class are well known for their superior balance of physical strength properties, impact resistance and abrasion resistance and thermal stability. Nylon 610 is of particular interest of the modification of cotton textiles as it shares these qualities and offers additional toughness over the more common types 66 and 6; at the expense of some loss of heat resistance it is also readily available commercially for a variety of end product applications. Like other polyamides it is conventionally prepared by polycondensation at elevated temperatures. It can also be formed at the interface between a solution of a diacid chloride in a water immiscible organic solvent and a water solution of a diamine (Interfacial Polymerization). Specifically, nylon 610 is prepared at ambient temperatures by reacting sebacoyl chloride dissolved in water immiscible organic solvent (e.g., tetrachloroethylene) with an aqueous solution of hexamethylene diamine (HMDA). The reaction can be represented as follows:



Pertinent process parameters at a fixed temperature are listed as purity and concentrations of the reactants; transfer rates of the reactants; precipitation rate (solubility) of the polymer formed; partition potential of the reactants; concentration ratios of the phases; stirring; hydrolysis of the acid halide; transfer rate of the salt; fluid and polymer solution viscosities; polarity of solvent and interfacial energy barriers. ⁽²⁹⁾ Previous work has shown that the rate of hydrolysis of the acid halide and the proper deposition of the by product hydrochloric acid constituted the major process problem areas.

As indicated the experimental investigations to be discussed below are based on an improved version of the previously developed so-called vapor liquid phase interfacial Nylon 610 polycondensation process which is summarized below. Accordingly conditioned cotton cloths were treated to obtain Nylon 610 polymer coating add-on in varying amounts and then reacted with methylamide and diisocyanates as cross linking agents. Formaldehyde and formaldehyde donors react at elevated temperatures with polyamides as well as cotton cellulose. ⁽³⁷⁻⁴¹⁾ The use of aliphatic diisocyanates as candidate cross linking agents is of particular interest in view of recent claims as to the greater strength retention of diisocyanate crosslinked cotton cloths compared to conventional methylolamide cross linking agents, ⁽⁴²⁾ and their ability to also cause cross linking of polyamides. ⁽⁴³⁾ The specific aliphatic diisocyanate employed was

selected on the basis of its high degree of chemical stability and relatively better hydrolysis resistance at ambient temperatures (slower hydrolysis rates). Aliphatic diisocyanates are reported to cause minimum yellowing upon aging compared to their aromatic counterparts such as TDI. The products were then evaluated in terms of pertinent performance characteristics.

Experimental:

The following is a list of the more significant chemicals which were utilized for these experiments together with the suppliers employed:

hexamethylenediamine (99.8% pure); Celanese Chemical Co., New York, N.Y.

sebacoyl chloride (99.6% pure); Eastman Chemical Co., Rochester, N.Y.

Permafresh 183, Catalyst X-4, Mykon SF; Sun Chemical Co., Wood River Junction, R.I.

Triton X-100; Triton X-405; Rohm & Haas Co., Philadelphia, N.Y.

TMDI (2,2,4)-(2,4,4) Trimethylhexamethylene diisocyanate;

Scholven-Chemie A.G. (distributor H. Stinnes
Chemical Co., New York, N.Y.

IPDI (3 isocyanato-3,5,5 Trimethylcyclohexyl isocyanate);

Scholven-Chemie A.G. (distributor H. Stinnes
Chemical Co., New York, N.Y.

dibutyltin diacetate (cp grade); Eastman Chemical Co., Rochester, N.Y.

The fabrics employed throughout this investigation were 80 x 80 desized, bleached, mercerized cotton print cloths (Style 400 W) obtained from Testfabrics Inc., New York, N.Y. Fabric samples of 10" x 6" size

were wet from the variously polymer treated cloths for use in the performance evaluation tests to be described below.

The vapor-liquid interfacial polycondensation apparatus (Figure 39) used for this investigation consisted of four chambers containing successively (1) a liquid bath of one of the reactants - sebacoyl chloride dissolved in carbon tetrachloride; (2) a positive pressure chamber; (3) a chamber containing vapor of the other reactant - the diamine - provided with a vapor dispensing mechanism; and (4) a water wash chamber. The residence time in each could be controlled by adjustable roller mechanisms in the individual chambers. A constant torque, variable speed motor pulls the sample through the chambers at a preset rate to wind-up on a second, "product" reel.

Type 80 x 80 cotton print cloth samples (9" x 20') were dried to constant weight at 80°C in an air circulating oven and suitably positioned and fastened on the starter roll shown in Fig. 39, connected to a "leader" cloth for subsequent processing. The samples were first pulled through the chamber containing from 10-20 w % solutions of sebacoyl chloride in carbon tetrachloride. They remained immersed in this solution for time periods ranging from 10-30 seconds depending as noted above upon the speed of the motor. The sample cloth was then pulled through a positive nitrogen chamber (to prevent back mixing) into the hexamethylene-diamine (HMDA) chamber. Hexamethylenediamine vapor was transported to this chamber with nitrogen as a carrier gas (1.0 liter/min.) by bubbling it through a reservoir of hot diamine liquid (170-180°C). (HMDA reservoir not shown in Fig. 39. The polyamide polymer coated cloth

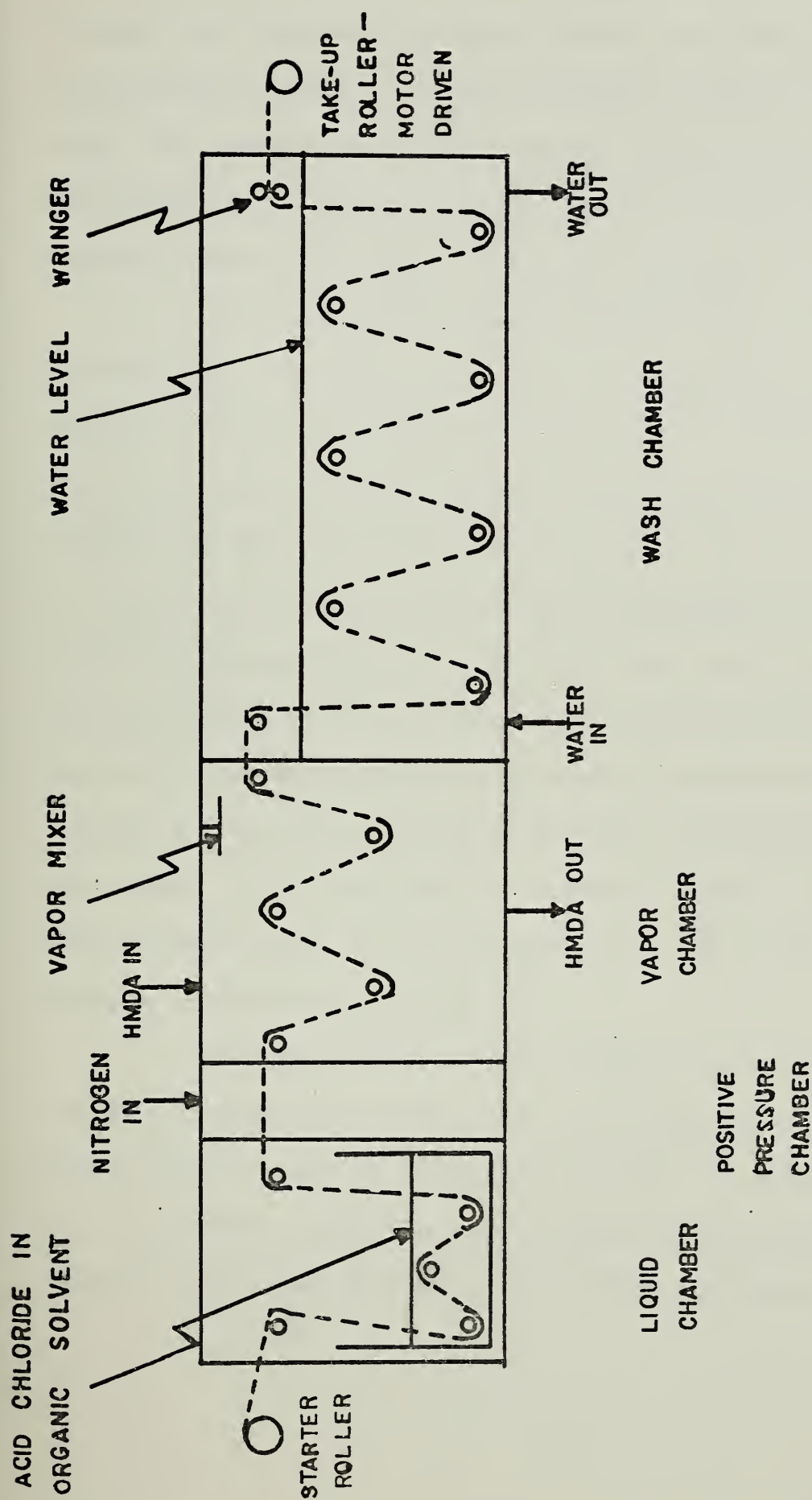


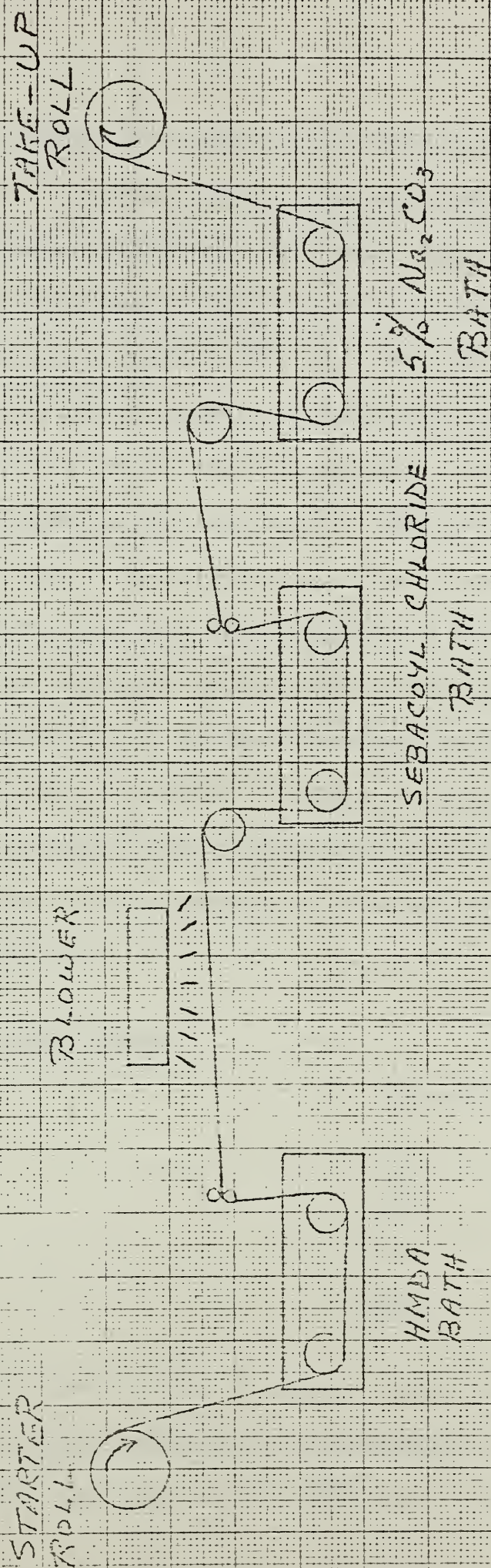
FIG. 39. VAPOR-LIQUID INTERFACIAL
POLYCONDENSATION APPARATUS
FOR COATING CLOTH SAMPLES
WITH NYLON 610
(CONTINUOUS PROCESS)

samples were then washed in the so-called wash chamber which contained a dilute sodium carbonate for neutralization of by product hydrochloric acid. The samples were further washed in hot water in a standard washing machine for 2-3 minute cycles, dried to constant weight etc. and polymer add-ons determined by appropriate weighings.

For comparison purpose all liquid phase interfacial polyamide condensations were also carried out. A schematic of the equipment is shown in Fig. 40. The same type of previously referred to cotton print cloth was dried to constant weight as detailed immediately above. The samples were then positioned and fastened on the starter roll, connected to a leader cloth, and pulled through a hexamethylenediamine solution containing various additives. They were then pulled past an air blower and immersed into a carbon tetrachloride solution of sebacyl chloride, from which they were pulled out to enter a neutralization tank containing a dilute aqueous sodium carbonate solution. The polymer coated samples were washed in hot water again in a standard washing machine for 2-30 minute cycles, dried to constant weight etc. and polymer add'ons determined by appropriate weighings.

As reported these polymer forming reactions result in the essentially instantaneous deposition of thermoplastic polyamides on cotton fibers at ambient temperatures without disadvantageously affecting cotton fiber physical strength properties but no gain in wrinkle recovery and related desirable cotton fabric performance properties.

FIG. 40: SCHEMATIC OF LIQUID / LIQUID INTERFACIAL
POLYCONDENSATION FOR CONTINUOUS NYLON
COATING OF COTTON CLOTH



A primary objective of cross linking finishing treatments for cotton fabrics is to provide them with improved shape-holding properties such as wrinkle resistance, wash wear characteristics and dimensional stability while minimizing the loss of durability of cotton in so-called permanent press garments.⁽¹⁸⁾ The reduction in fiber toughness and fixation of the fabric geometry brought about presumably by the cross linking of the cellulose are directly related to the lowered durability of such cross linked cotton fabrics.⁽¹⁹⁾ When the polyamide polymer treated cotton cloths were to be subjected to cross linking treatments for the above stated purpose, they were first weighed and then subjected to the action of either the catalyzed methylolamide cross linking agent system (Permafresh 183 and Catalyst X 4) or the diisocyanate cross linking agent system (TMDI catalyzed with dibutyltin diacetate; uncatalyzed) at elevated temperatures. In all cotton control samples were also cross linked.

Specific cross linking systems and treating conditions are summarized immediately below.

Methylolamide cross linking system

Permafresh 183	90 parts by wt.
Mykon SF	40 " " "
Triton X-405	20 " " "
Catalyst X-4	20 " " "
Water	2000 " " "

The weighed polymer coated or control cotton fabrics were immersed in the cross linking solution for approximately 15 minutes, dried at 80°C for 10 min. and cured at 170-180°C for 1.5 minutes.

The samples were then repeatedly washed, dried to constant weight etc. Certain pertinent physical properties were then measured on the cross linked samples including tensile characteristics, tear, wrinkle recovery and abrasion in accordance with applicable ASTM test procedures.

Diisocyanate cross linking system

TMDI diisocyanate	30 parts by wt.
dimethylformamide (anhydrous)	300 " " "
dibutyltin diacetate (optional)	1.5 " " "

The carefully dried weighed polymer coated or control cotton fabrics were immersed in this cross linking solution for approximately 15 minutes. Excess liquid was removed and curing effected at 140°C for about 2 hours in an air circulating oven. The samples were then repeatedly washed, dried to constant weight etc. Certain pertinent physical properties were then measured on the cross linked samples including tensile characteristics, tear, wrinkle recovery and abrasion resistance in accordance with applicable ASTM test procedures. It should be noted that DMF solutions of diisocyanates have previously been reportedly used for the cross linking of cotton cellulose fabrics.⁽⁴⁴⁾

It should be understood that both the methylolamide and diisocyanate cross linking treatments can be effected with many time-temperature-reagent concentration variations. The subsequent data should be considered preliminary indications of such cross linking treatments on Nylon 610 polyamide modified cotton fabrics.

The factors which affect the amount of polymer pick-up with the so-called vapor liquid interfacial polycondensation system for Nylon 610

polyamide have been previously considered. They include the concentration of the acid chloride and the hexamethylenediamine, the latter being a function of its flow rate and the contact time of the traveling cotton cloth with these reactants. The specific data reported in Table 22 apply to a sebacoyl chloride concentration from 10-20 wt. % and a nitrogen carrier gas flow rate of 1 liter/minute with the hexamethylene diamine reservoir maintained at 170-180°C in the absence of air, the greater polymer pickup being obtained with the higher sebacoyl chloride concentration. These runs were carried out always with the presence of excess hexamethylene diamine.

The polymer formation with the all liquid phase interfacial polycondensation reaction is likewise affected by the sebacoyl chloride and hexamethylenediamine concentrations as well as the contact time of the cotton cloth samples with each reactant. The cotton cloth samples were pulled through the system depicted in Fig. 40 at a rate of approximately 4"/min. The contact time of the cloth with each reactant was in the order of 1 minute. The effects of variations in the hexamethylenediamine and sebacoyl chloride solution concentrations on nylon polymer add'on are shown in Figs. 41 and 42. A wetting agent (Triton X 100) a softener (Mykon SF) and a neutralizer (sodium carbonate) were added to the hexamethylenediamine solution in various small amounts to promote wetting, enhance final product hand and help neutralize the later formed by product acid. Experiments not reported below, were conducted with various concentrations of different wetting agents etc. The specific hexamethylenediamine solution compositions employed to obtain the data shown in Figs. 41 and 42 are representative of typical suitable formulations.

FIG. 11: NYLON WT. % ADD-ON VS.
HMDA CONCENTRATION

HMDA SOLUTION		CONSTANT SEBACOYL CHLORIDE SOLUTION	
100 PARTS	H ₂ O	2.0 CC	SEB. CHLORIDE
X PART	HMDA		
8.0 PARTS	Na ₂ CO ₃	100 CC	CCl ₄
1.0 PARTS	TRITON X-100		
1.25 PARTS	MYKON SF		

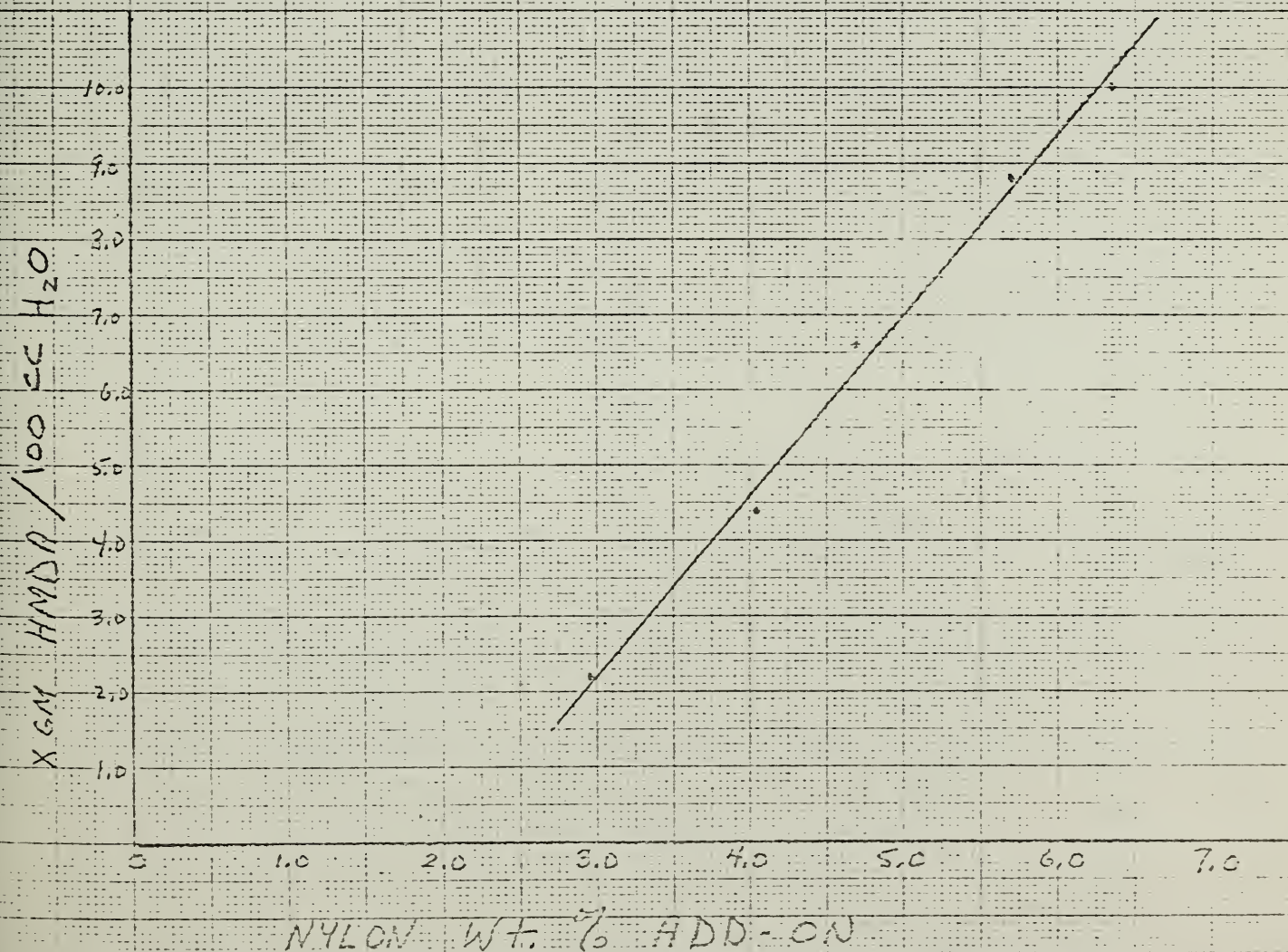


FIG. 42: NYLON WT. % ADD-ON VS.

SEBACOYL CHLORIDE CONCENTRATION

CONSTANT HMMA SOLUTION

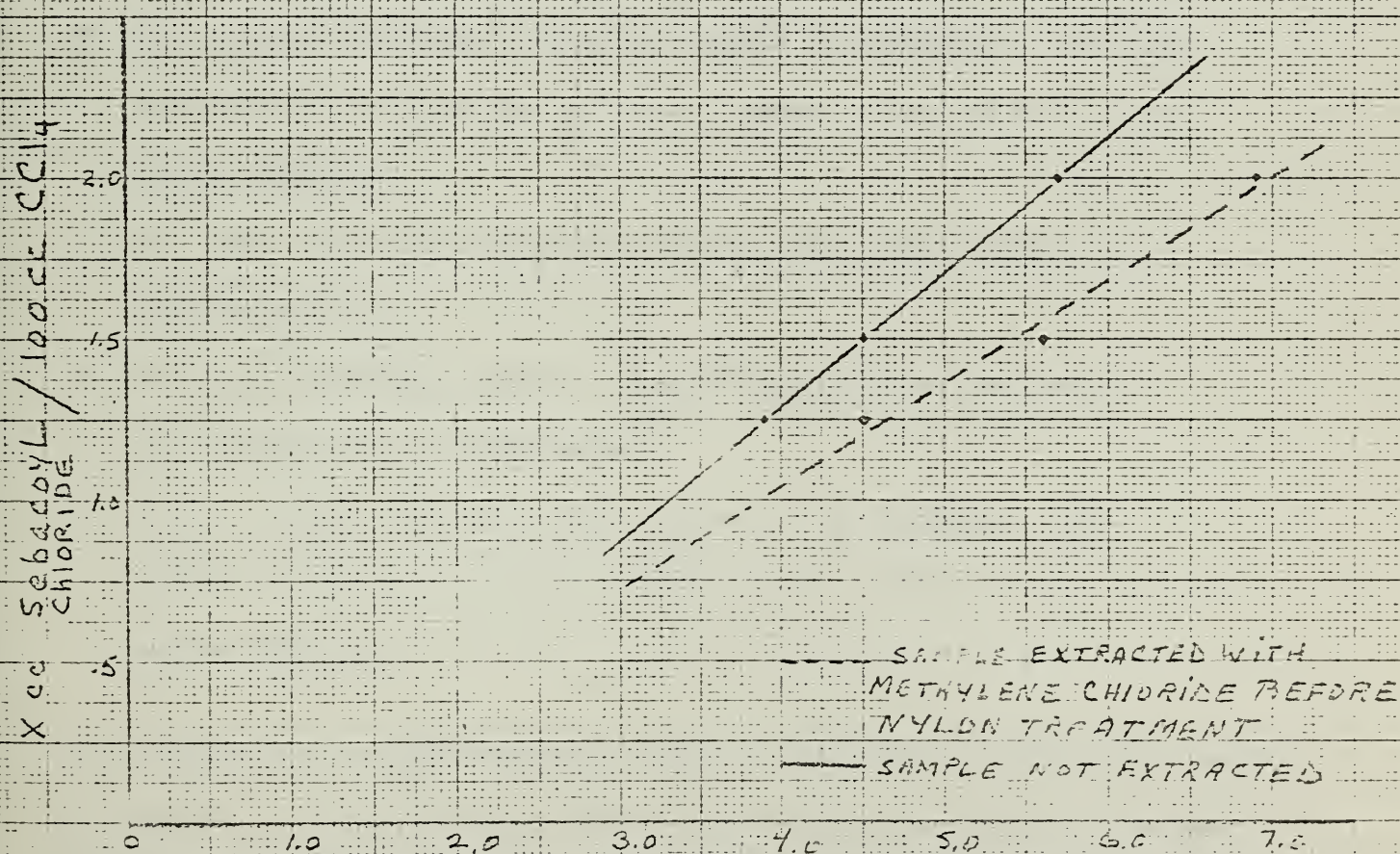
100 PARTS H_2O

4.4 PARTS HMMA

8.0 PARTS Na_2CO_3

1.0 PARTS TRITON X-100

1.25 PARTS MYKON SF



NYLON WT. % ADD-ON

The relations between the Nylon 610 polymer add-on and certain pertinent physical properties of the Nylon 610 polymer deposited cotton fabrics are shown in Table 22. Similar information for variously cross linked Nylon 610 polymer modified cotton fabrics are given in Table 23. Data are presented for both vapor/liquid and all liquid phase interfacial polycondensation reaction techniques.

Considerations of the data in Table 22 shows clearly the following:

- a) The vapor/liquid and all liquid phase interfacial polycondensation techniques give similar results at comparable polymer add-ons.
- b) The tensile strength properties remain substantially unchanged with polymer add-ons up to 8 wt. % based on the weight of the cotton fabrics.
- c) The tear strength increases markedly with larger amounts of polymer add-on.
- d) Abrasion resistance shows a significant gain as the amount of polymer add-on is increased.
- e) Shape holding characteristics appear to be unchanged with polymer add-ons up to 8 wt. % based on the weight of the cotton fabrics.

The results can be summarized in terms of retention of physical strength properties, no gain in shape holding characteristics (wrinkle recovery test), improvements in tear strength and some moderate gain in abrasion resistance (note that this trend was noted with two different test methods i.e. Stoll Flex and Inflated Diaphragm).

Table 22. Interfacial polycondensation of Nylon 610 on cotton fabrics

Physical properties of polymer coated cotton fabrics (80x80 print cloths)

A. Liquid/Vapor Technique

Sample	% Nylon add-on	Breaking Strength (lb) ⁽¹⁾ (% Strength Retention)		Tear strength ⁽²⁾ gms		Abrasion cycles to failure (3)		Wrinkle Recovery ⁽⁴⁾ W + F	
		Warp	Fill	Warp	Fill	Warp	Fill	Dry	Wet
Control	-	52 (100)	33 (100)	530	805	495	410	190	143
P-29-1	.9	47.8 (92)	32 (97)	575	822	670	510	198	164
P-29-2	1.6	49.9 (96)	32 (97)	608	873	800	530	184	168
P-30-1A	4.2	50.5 (97)	31.6 (96)	675	952	1320	1090	183	160
P-30-1B	8.1	45.3 (87)	28 (85)	935	1055	1580	1170	179	168

(1) ASTM D 1682-64 (Average of 3 runs)

(2) ASTM D 1424-63 (Average of 5 runs)

(3) ASTM D 1175-61T (Average of 5 runs)

(4) ASTM D 1295-60T (Average of 5 runs)

Table 22. (continued)

B. Liquid/Liquid Technique

Sample	% Nylon add-on	Breaking Strength (lb)(1)		Tear Strength (2)		Abrasion Cycles(3)		Wrinkle Recovery (4)	
		Warp	Fill	Warp	gms	Fill	to failure	Dry	Wet
Control	-	56.2 (100)	28.7 (100)	544	845	100	154	149	
F-43-1	1.1	51.7 (92.1)	26.3 (91.8)	535	630	105	189	155	
F-43-2	3.2	50.7 (90.3)	24.7 (86.2)	650	910	112	192	185	
F-43-3	5.0	49.8 (88.7)	25.8 (90.1)	690	1410	131	203	187	
F-44-1	6.0	53.6 (95.5)	27.4 (95.5)	829	1082	145	212	205	
P-44-2	8.7	54.1 (96.3)	26.0 (90.1)	950	1174	130	200	175	

(1) ASTM D 1682-64 (Average of 5 runs)

(2) ASTM D 1424-63 (Average of 5 runs)

(3) ASTM D 1175-64T (Average of 5 runs)

(4) ASTM D 1295-60T (Average of 5 runs)



Table 23. Interfacial polycondensation of Nylon 610 on cotton fabrics with subsequent cross linking.

Physical properties of coated cotton fabrics (80 x 80 print cloth)

A. Liquid/Vapor Technique

Methylolamide Type Cross Linker (Permafresh 183)

Sample	% Nylon add-on	% Permafresh add-on	-Breaking Strength (lb)(1)		Tear Strength(2) gms	Abrasion(3) cycles to failure	Wrinkle Recovery(4) W + F	
			Warp	Fill			Dry	Wet
Control	-	-	56.2 (100)	28.7 (100)	544	100	154	149
P-45-2	-	4.4	34.0 (60.5)	14.9 (52.8)	358	68	207	281
P-53-1	-	6.5	27.2 (48.4)	13.8 (48.1)	294	52	282	259
P-30-2	4.2	7.5	38.7 (68.9)	19.8 (69.0)	362	83	276	265
P-30-3	4.2	9.5	37.3 (66.4)	19.3 (67.3)	312	80	288	274
P-30-4	4.2	2.9	38.9 (69.3)	19.5 (68.0)	400	96	265	255
(1)	ASTM D 1682-64 (Average of 5 runs)		(3)		ASTM D 1175-64T (Average of 5 runs)			
(2)	ASTM D 1424-63 (Average of 5 runs)		(4)		ASTM D 1175-64T (Average of 5 runs)			

Table 23 (continued)

B. Liquid/Liquid Technique

I. Methylol Amide Type Cross Linker (Permafresh 183)

Sample	% Nylon add-on	% Perma- fresh add-on	Breaking Strength (lb.) ⁽¹⁾		Tear Strength ⁽²⁾ gms	Abrasion ⁽³⁾ cycles to failure	Wrinkle Recovery ⁽⁴⁾	
			Warp	Fill			Dry	Wet
Control	-	-	56.2 (100)	28.7 (100)	544	100	154	149
P-45-2	-	4.4	34 (60.5)	15.1 (52.8)	358	68	287	281
P-53-1	-	6.5	27.8 (49.4)	13.8 (48.1)	294	5.2	282	269
P-53-2	3.3	9.3	33.2 (59.2)	13.9 (66.1)	355	82	288	275
P-53-3	5.0	8.3	34.1 (60.7)	19.2 (67.0)	317	83	285	280
P-45-1	6.0	2.9	37.8 (67.2)	15.3 (65.7)	390	91	297	282
P-53-4	6.3	3.9	39.8 (70.7)	20.2 (70.4)	438	85	281	259

(1) ASTM D 1682-64 (Average of 5 runs)

(2) ASTM D 1424-63 (Average of 5 runs)

(3) ASTM D 1175-64T (Average of 5 runs)

(4) ASTM D 1295-60T (Average of 5 runs)

Table 23 (continued)

II. Diisocyanate Type cross linker (TMDI) (See Appendix)										
Sample	% Nylon Add-on	% Diiso cyanate Add-on	Breaking Strength (lb)		(1)Tear Strength		Abrasion (3)	Wrinkle Recovery(4)		
			% Strength Retention		gms	Cycles to failure		Dry	Wet	
			Warp	Fill			Warp			
Control	-	-	51.8 (100)	26.3 (100)	416	790	93	162	150	
P-89-2	-	5.9	33.7 (65)	18.9 (72)	300	522	80	259	252	
P-104-2A*	4.9	9.8	45.5 (88)	22.6 (86)	334	656	147	202	195	
P-104-B	4.9	9.1	42.4 (82)	22.1 (84)	330	660	103	262	259	
P-104-3	4.9	7.1	39.4 (76)	19.7 (75)	322	640	101	258	248	
P-104-4	4.9	-	55.9 (108)	26.3 (100)	704	1230	118	183	175	
(1)	ASTM D 1682-64 (Average of 5 runs		(3) ASTM D 1175-64T (Average of 5 runs)							
(2)	ASTM D 1424-63 (Average of 5 runs)		(4) ASTM D 1295-60T (Average of 5 runs)							

* Contained dibutyltin diacetate catalyst in crosslinking formulation

The information which can be developed from experiments relating to the evaluation of Nylon 610 polyamide coated crosslinked cotton fabrics as presented in Table 23, is summarized as follows:

- a) the vapor liquid and all liquid phase interfacial polycondensation techniques give similar results at comparable polymer add-ons with the same cross linking agent.
- b) treatment of Nylon 610 polymer coated cotton fabrics with varying amounts of Permafresh 183 cross linking agent
 - b-1 does reduce physical strength properties but not to the same extent as is the case with uncoated crosslinked fabrics at comparable cross linking agent add-ons.
 - b-2 tear strengths are reduced but not to the same extent as for uncoated cross linked fabrics, again at comparable polymer add-ons.
 - b-3 abrasion resistance values are maintained to a much higher degree than for uncoated cross linked fabrics at comparable polymer add-ons.
 - b-4 shape holding properties (wrinkle recovery data) are of the same order as those obtained with unmodified Permafresh 183 coated cotton fabrics.
- c) treatment of Nylon 610 polymer coated cotton fabrics with TMDI cross linking agent
 - c-1 does reduce physical strength properties but not to the same extent as is the case with uncoated cross linked fabrics at comparable polymer add-ons; furthermore, the strength losses are less than those experienced with the Permafresh 183 cross linking treatment.

- c-2 tear strengths are reduced but not to the same extent as for uncoated cross linked fabrics, again at comparable polymer add-ons.
- c-3 abrasion resistances were improved in all cases over the uncoated cross linked cotton fabrics.
- c-4 shape holding properties are improved; use of a catalyst in the diisocyanate cross linking formulation significantly enhances abrasion resistance but does not improve wrinkle recovery.

Consideration of these results indicates very much the same effects as described previously for the Permafresh 183 cross linking agent system except that the diisocyanate cross linking treatment without catalyst appears to offer increased strength retention and other associated desirable properties. It must be emphasized that these data are preliminary and additional experiments must be carried out both for confirmation and optimization. These proposed experiments should include evaluation of various other aliphatic diisocyanates such as hexamethylene diisocyanate and 3-isocyanato-methyl 3,5-trimethylcyclohexylisocyanate with different catalysts at a number of curing conditions (time-temperature relationships). Also as indicated above the degree of cross linking of the nylon surface polymers if any, should be investigated. The best results obtained with Nylon 610 polymer coated TMDI diisocyanate cross linked cotton fabrics show strength retentions in the order of 75%, essentially unchanged tear strength, improved abrasion resistance and wrinkle recoveries in the order of 260 at a total add-on of around 12%.

A considerable amount of time was spent on microscopic studies in order to develop pertinent information relative to the location character and structure of these Nylon 610 polymer deposits on cotton fabrics before and after cross linking agent treatments. Sections of such fibers were differentially stained with Eastman Fast Blue B-GLF and other dyestuffs and embedded in an acrylic polymer medium as described in previous reports in order to visually locate the polymer deposits. This work was unsuccessful because of insufficient polymer add-ons (8% maximum).^{*} Larger polymer weight add-ons would facilitate differential staining but such heavy polymer deposits would tend to disadvantageously affect polymer hand etc.

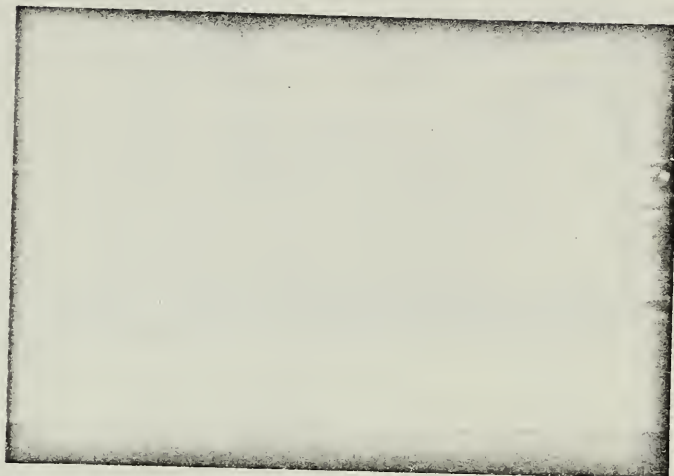
The Nylon 610 polymer coated cotton fabrics are not cross linked as is confirmed by the solubility of the cotton in cupriethylenediamine leaving behind Nylon polymer residues, Fig. 43. The Nylon coated methylolamide and diisocyanate cross linked cotton fabrics are completely insoluble in cupriethylene diamine. Photographic evidence of this insolubility in the cellulose solvent is shown in the appended pictures, Fig. 44. As noted additional experimental studies are in progress to more clearly differentiate the effects of the cross linking agents on the Nylon polymer coatings and the cotton cellulose. The identity of the Nylon 610 polymer deposits was repeatedly confirmed by infrared spectrometry of the residual nylon deposit and is shown in Fig. 45.

* M. Rollins of USDA confirms difficulties of obtaining good differential stains with relatively low polymer add-ons - conversation June 1969.





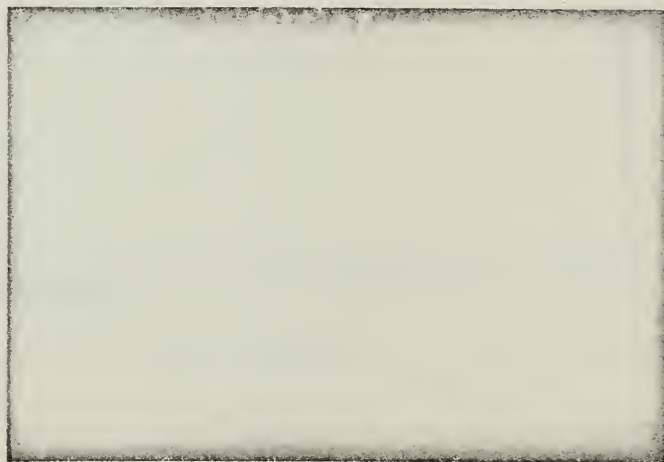
A. X 125



B. X 500

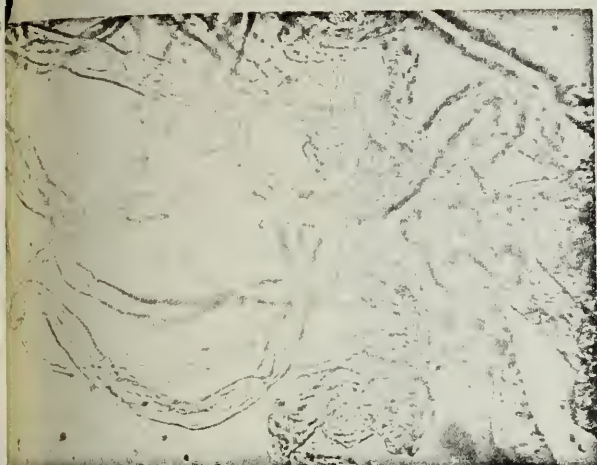


C. X 500



D. X 500

Fig. 43. Nylon Coated Cotton Samples - not cross linked -
Residual Nylon after 1 hr. in cuene.



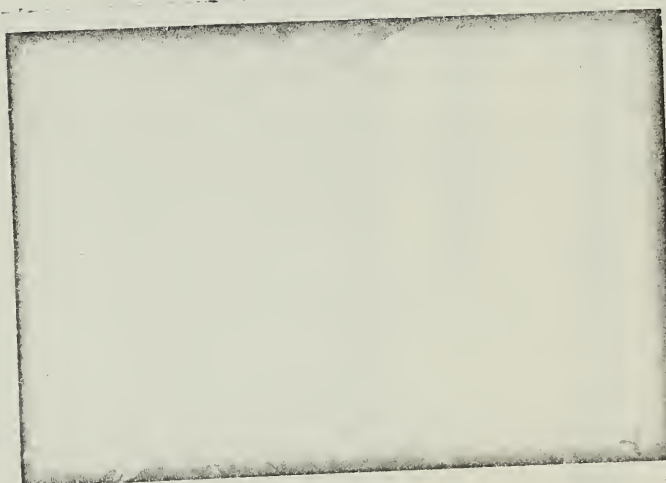
A. X 125



B. X 125



C. X 125



D. X 125

Fig. 44 (A & B): TMDI treated cotton samples with no nylon;
after 1.5 hrs. cuene - 6% TMDI add-on.

(C & D): TMDI treated nylon coated cotton samples;
after 1.5 hrs. cuene - 4.2% nylon add-on, approx. 8%
TMDI add-on.

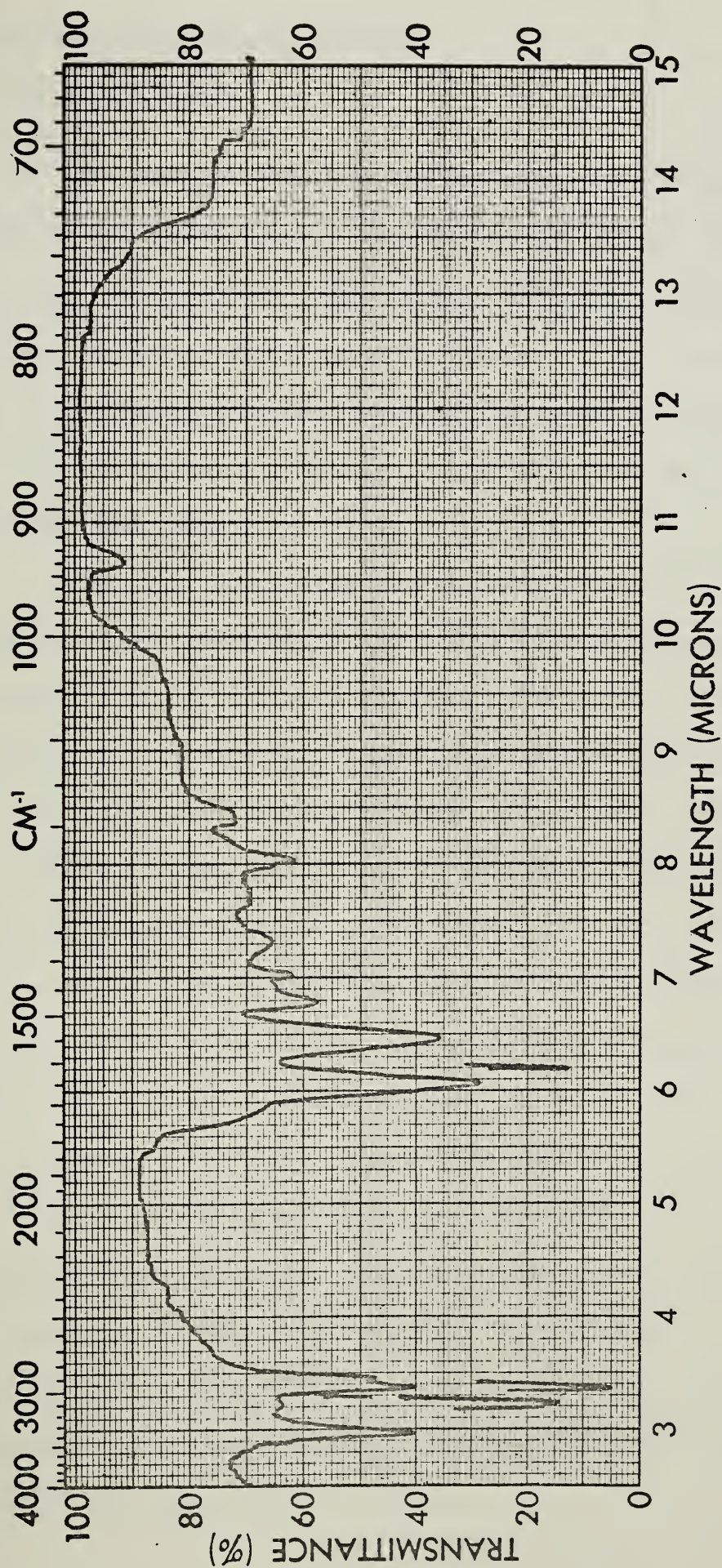


Fig. 45. I.R. Spectrum of Nylon 610 Coated Cotton Ground in KBr Pellet

Diisocyanate cross linked polyamide
coated cotton fabrics.

The specific diisocyanate employed for the treatment of the polymer coated cotton fabrics was (2,2,4)-(2,4,4) trimethyl hexamethylene diisocyanate (TMDI) which has also been described in that report.

The major variables which were investigated in this experimental study were the treatment conditions such as TMDI concentration, time and temperature with and without a catalyst for promotion of the desired reaction (dibutyltin diacetate).

The Nylon 610 polymer coated cotton fabrics were treated with a dimethylformamide solution of 2,2,4-(2,4,4) trimethylhexamethylene-diisocyanate with and without dibutyltin diacetate catalyst. This particular diisocyanate had been employed successfully in the previously described exploratory studies and was originally selected on the basis of its unusually low volatility* and a reactivity similar to that exhibited by hexamethylenediisocyanate - a combination of properties which simplifies handling and processing characteristics with this compound. Different quantities of the 2,2,4-(2,4,4) trimethylhexamethylenediisocyanate and in certain cases dibutyltin diacetate were dissolved in dimethylformamide to produce solutions of various known diisocyanate and catalyst concentrations. Cotton fabric samples with established Nylon 610 polymer contents were immersed in these solutions. Immersion times in the order of 15 minutes were employed. A typical diisocyanate treating solution consisted of 30 pts. by wt. of TMDI, 300 pts. by wt. of anhydrous DMF and 1 pt. by wt. of dibutyltin diacetate. Excess liquid was then removed and the thusly

* boiling point 140-148°C at 10 mm Hg

treated cotton cloth samples heated for predetermined temperature/time schedules in order to effect reaction. The samples were then repeatedly washed, dried to constant weight, etc. and subjected to various fabric performance evaluation tests. These included tensile characteristics, tear, wrinkle recovery and abrasion resistance in accordance with applicable ASTM test procedures. It should be noted that DMF solutions of diisocyanates such as hexamethylenediisocyanate, have previously been reportedly used for the cross linking of cotton cellulose fabrics. In all cases cotton control samples without the polyamide deposits were also treated with the same diisocyanate for comparison purposes. All the TMDI cross linked cotton cloth samples were found to be insoluble in cuene.

The following is a list of the more significant chemicals which were utilized in these experiments together with the names and addresses of the suppliers employed; there are of course alternative sources of most of these supplies which can be utilized if desired.

hexamethylenediamine (99.8% pure); Celanese Chemical Co., New York, N.Y.

sebacoyl chloride (99.6% pure); Eastman Chemical Co., Rochester, N.Y.

Triton X-100; Triton X-405; Rohm & Haas Co., Philadelphia, Pa.

TMDI (2,2,4)-(2,4,4) Trimethylhexamethylene diisocyanate

Scholven-Chemie A.G. (distributor H. Stinnes Chemical Co.,

New York, N.Y.

dibutyltin diacetate (cp grade); Eastman Chemical Co., Rochester, N.Y.

As noted the fabrics employed throughout this investigation were 80 x 80 desized, bleached, mercerized cotton print cloths. Fabric samples of 10" x 6" size were cut from the variously polymer treated cloths for use in the performance evaluation tests to be described below.

The experimental data which were obtained in studies of the treatment of Nylon 610 polyamide coated cotton fabrics with 2,2,4-(2,4,4) trimethylhexamethylene diisocyanate (TMDI) are summarized in Table 24. The experiments described employed cotton fabrics with approximately 4-5% weight add-ons of Nylon 610 polyamide and resulted in diisocyanate add-ons ranging from 4.5-10%, based upon the weight of the cotton fabrics. The effect of changes in the concentration of the TMDI in the DMF solution with and without dibutyltin diacetate catalyst on the diisocyanate add-on of the polymer coated cotton fabrics is shown in Fig. 43. In Figures 44 and 45 data are presented which show the effect of variations in curing times from 1/2 to 3 hours and curing temperature changes from 100 to 175°C respectively on the diisocyanate weight gain of the polyamide coated cottons, again with and without the dibutyltin diacetate catalyst. The curing conditions which were employed for the experiments summarized in Fig. 43, were 140°C for 1 hour. For the experiments described in Fig. 44 the concentration of the TMDI in the DMF solution was 10 pts. per 100 pts. DMF and the curing temperature amounted to 140°C. The TMDI concentration was the same and the curing time fixed at 1 hour for the data developed in Fig. 45. Microscopic studies for elucidation of the location and structure of the polymer deposits and the characteristics of the cross linked polymer/fiber composites are in progress.



Table 24. Interfacial polycondensation of Nylon 610 on cotton fabrics and subsequent crosslinking with TMDI diisocyanate physical properties of polymer coated cotton fabrics (80 x 80 print cloth)

Sample	% Nylon Add-on	% Diisocyanate Add-on	Breaking Strength (lb.) (1)		Tear Strength (2)		Abrasion (3) Cycles to failure	Wrinkle Recovery (4)	
			Warp	Fill	Warp	gms. Fill		Dry	Wet
Control	-	-	51.8 (100)	26.3 (100)	416	790	93	162	150
89-2	-	5.9	33.7 (65)	18.9 (72)	300	522	80	259	252
89-2A*	-	6.5	30.5 (58.7)	18.0 (68.5)	285	540	74	242	235
104-2A*	4.9	9.8	45.5 (88)	22.6 (86)	334	656	147	202	195
104-3	4.9	7.1	39.4 (76)	19.7 (75)	322	640	101	258	247
104-4	4.9	-	55.9 (108)	26.3 (100)	704	1230	118	183	175
113-2	3.9	5.2	33.6 (65)	16.5 (63)	262	510	67	279	272
113-3	3.9	5.8	33.2 (64)	17.0 (65)	294	585	72	276	263
113-5*	3.9	8.0	41.8 (81)	21.0 (80)	336	650	107	212	217

(1) ASTM D 1682-64 (Average of 5 runs)

(2) ASTM D 1424-63 (Average of 5 runs)

(3) ASTM D 1175-64T (Average of 5 runs)

(4) ASTM D 1295-60T (Average of 5 runs)

* Contained dibutyltin diacetate catalyst in crosslinking formulation.



Interfacial polycondensation of Nylon 610 on cotton fabrics and subsequent crosslinking with TMDI diisocyanate physical properties of polymer coated cotton fabrics (80 x 80 print cloth)

Table 24
(cont.)

Sample	% Nylon Add-on	% Diisocyanate Add-on	Breaking Strength (lb.) (1)		Tear Strength (2)		Abrasion (3) Cycles to failure	Wrinkle Recovery (4) W + F	
			Warp	Fill	Warp	Fill		Dry	Wet
113-6*	3.9	6.9	39.2 (76)	19.2 (73)	320	610	108	227	220
115-1	3.9	5.4	35.7 (69)	17.5 (67)	224	430	94	263	250
115-2	3.9	5.7	35.0 (68)	17.6 (67)	234	455	88	271	262
115-3	3.9	5.8	35.5 (69)	18.0 (69)	240	458	94	263	223
115-4*	3.9	6.6	40.2 (78)	20.4 (78)	294	562	119	226	214
115-5*	3.9	7.6	40.3 (78)	20.6 (78)	307	587	127	195	200
115-6*	3.9	7.9	43.9 (85)	22.0 (85)	323	638	124	206	200
115-7	3.9	6.1	38.4 (74)	19.1 (73)	272	550	118	269	267
115-9	3.9	4.8	34.9 (67)	17.5 (67)	211	405	91	275	267
115-10	3.9	4.5	34.4 (66)	16.5 (63)	221	416	109	273	275
116-1*	3.9	8.0	41.8 (81)	21.5 (82)	320	635	137	214	210
116-2*	3.9	6.9	40.6 (79)	20.3 (77)	333	622	135	228	230
116-3*	3.9	5.5	43.6 (84)	22.0 (84)	323	603	118	222	218

(1) ASTM D 1682-64 (Average of 5 runs)
(2) ASTM D 1424-63 (Average of 5 runs)

(3) ASTM D 1175-64T (Average of 5 runs)
(4) ASTM D 1295-60T (Average of 5 runs)

* Contained dibutyltin diacetate catalyst in crosslinking formulation.



FIGURE 43. PERCENT ADD-ON VS. TMDI
CONCENTRATION FOR REACTIONS AT
140°C FOR 1 HOUR

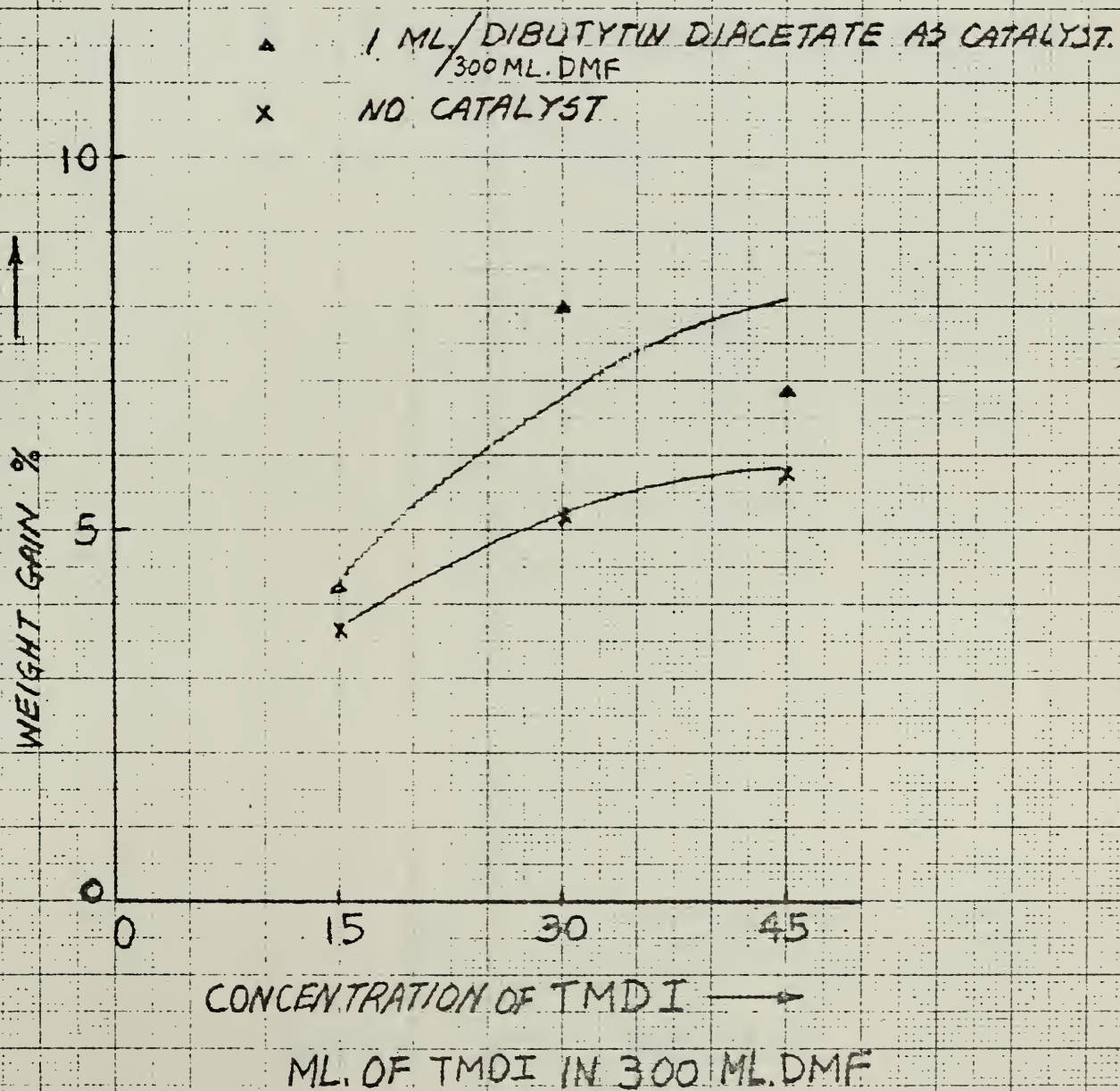




FIGURE 4. PER CENT ADD-ON VS CURING
TIME FOR REACTIONS AT 140°C AND
10pts TMDI / 100pts DMF CONCENTRATION

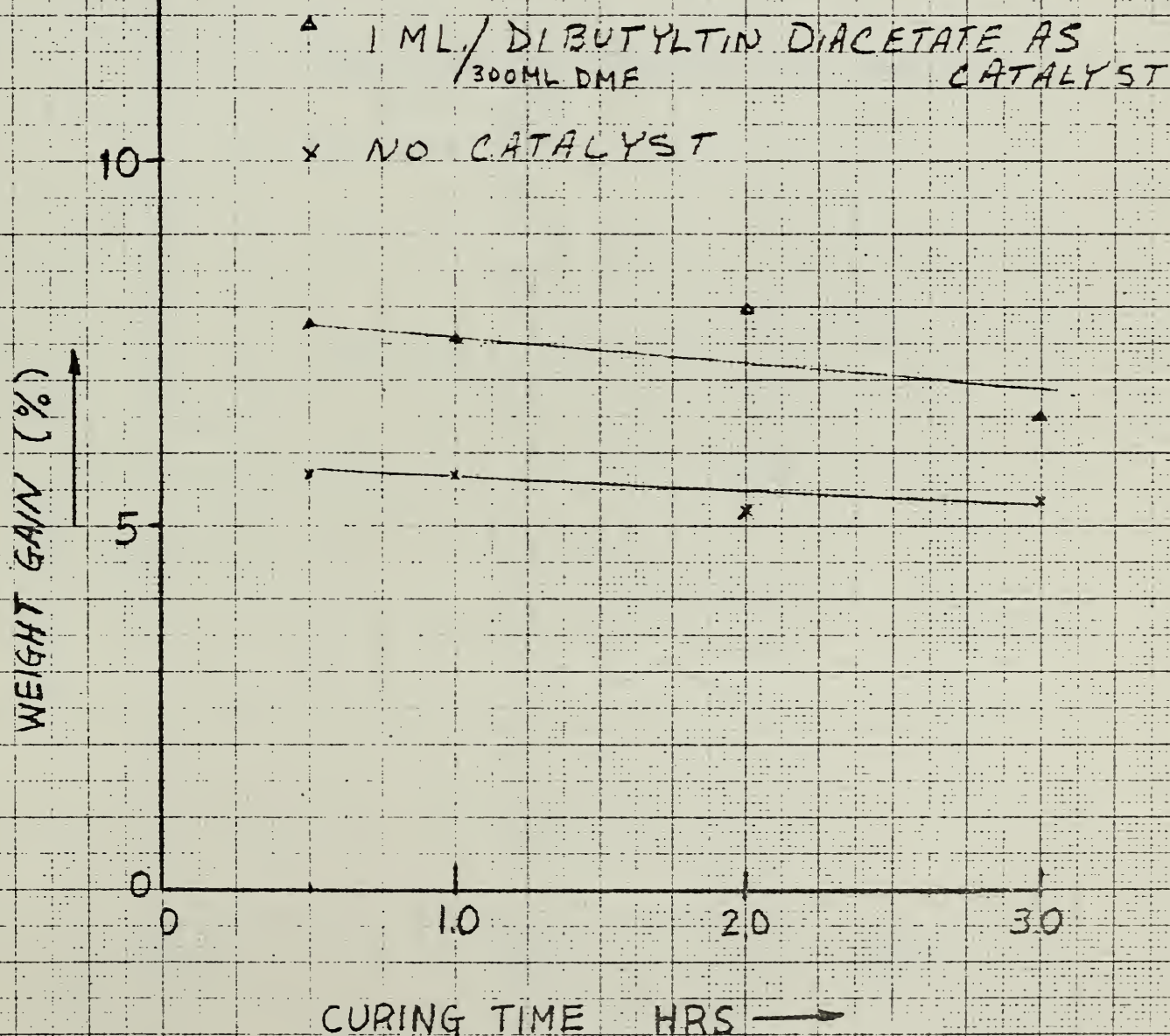
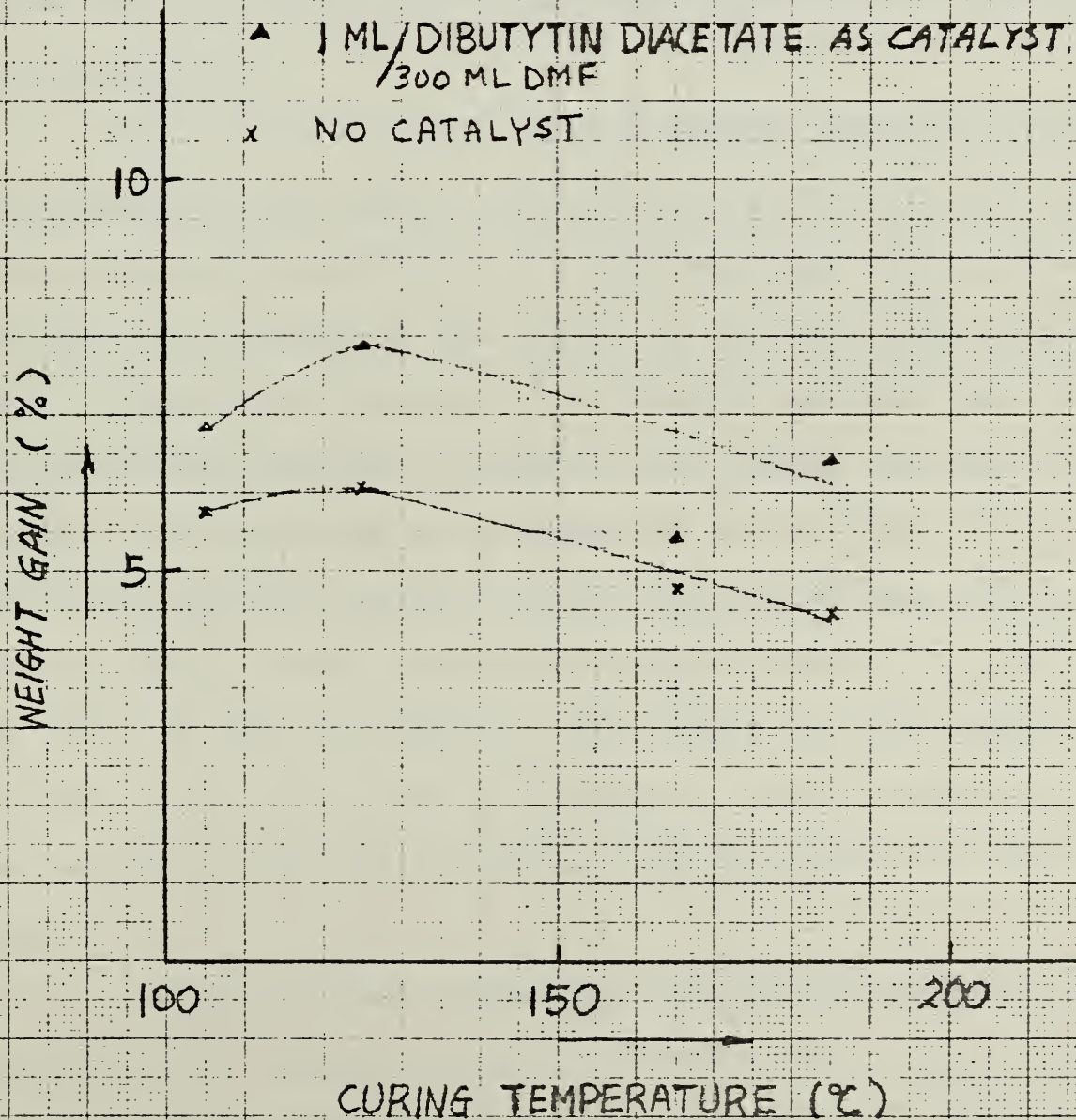




FIGURE 45. PER CENT ADD-ON VS CURING
TEMPERATURE FOR 1 HOUR REACTIONS
AT 10 PTS. TMDI / 100 PTS. DMF CONCENTRATION





The results obtained with TMDI treated cotton fabrics as shown in Table 24 may be summarized as follows. Cotton fabrics whose surfaces had been coated with the Nylon 610 polymer prior to the diisocyanate cross linking agent treatment showed greater retention of strength properties and abrasion resistance with roughly equivalent wrinkle recovery values than did the uncoated TMDI cross linked fabric samples even at somewhat higher cross linking agent add-ons within the range investigated.

The use of a catalyst such as dibutyltin diacetate to promote the diisocyanate cross linking reaction resulted in significant changes of the performance properties of such modified cotton fabrics. The data show that the employment of this catalyst in the diisocyanate treatment results in substantial increases of the abrasion resistance and the physical strength properties compared to test samples which were reacted with the same diisocyanate in the absence of this catalyst. The catalytically reacted samples did however show marked reductions in Monsanto wrinkle recovery measurements (compare samples 113-2 and 115-2 with 116-3 and 115-4, for example). The reasons for these results are not clear and are being further investigated. It may be speculated that this catalyst enhances the reactivity of the diisocyanate with the amide groups.

The Figures 43-45 inclusively show that higher TMDI concentrations in the DMF solution, presence of catalyst, higher curing temperatures all result in larger TMDI add-ons on the cotton fabrics.* Curing time

* Under the specific experimental conditions employed maximum TMDI add-on occurs in the 125°C range.



within the range studied does not appear to have a substantial effect on the TMDI add-on. More data are needed in order to establish clearly the effect of changes in the TMDI add-on from around 4.5-10% on such pertinent fabric performance parameters as Monsanto wrinkle recovery, tensile strength retention, tear strength and abrasion resistance. However as indicated above wrinkle recoveries are definitely affected adversely by the use of a catalyst in the diisocyanate cross linking agent system. Some of the more promising results obtained for 4 wt. % polyamide coated cotton cloth samples after being treated with 6% TMDI show wrinkle recoveries (W + F) of 269 dry and 267 wet with approximately 75% breaking strength retention and 118% of the original abrasion resistance (sample 115-7). Additional experiments are in progress in order to further develop the diisocyanate treatment concept without the use of a catalyst.

III. Conclusions

A. Polyethylacrylate

The above described experiments describe a reproducible and effective method for the vapor phase coating of cotton fiber cloth samples with polyethyl acrylate polymers. Conditions are described which result mainly in homopolymer formation. Pertinent physical properties of the polymer coated fiber samples have been experimentally evaluated. Wrinkle recovery values are somewhat improved but breaking strengths are substantially lowered. This may be due to the deleterious effect of SO₂ in presence of water (acid attack on cloth) and suggests evaluation of basic and/or neutral catalyst systems. Such systems, however, pose formidable difficulties to effective acrylate monomer polymerization.



Additional data presented for peroxide type catalyst demonstrate negligible strength losses. Experiments are described for methylolamide post-crosslinking of PEA coated cottons for upgrading of permanent press properties.

B. Polyglycidyl methacrylate

The above described experiments describe an effective method for the vapor phase encapsulation of cotton fiber cloth samples with glycidyl methacrylate polymers. Conditions are described which result in cross-linked homopolymer formation. The photomicrographs obtained during this investigation help explain the growth characteristics, degree of uniformity, and continuity of polymer coatings, and, also, the physical situation prevailing at the so-called fiber cross-over points. Abrasion resistance can be improved. The wrinkle recovery values are relatively unaffected. Breaking strength decreases as the % gross wt. gain increases. Heat and acid are, of course, detrimental to cellulose strength.

C. Polyoxymethylene

A novel reproducible and effective method for the vapor phase encapsulation of cotton fiber cloth samples with polyoxymethylene has been developed. Information on growth characteristics of polymer, degree of uniformity of polymer coatings can be obtained from a study of the photomicrographs. Typically, the polymer has a melting point of 165°C and a number average molecular weight of approximately 11,000. In sharp contrast to the acid catalyzed formaldehyde processes conventionally employed, the method developed in this investigation is unique in that it considerably increases the physical strength properties of cotton fabrics.



Acid catalyzed reactions involving the cross-linking of cotton with formaldehyde or reactive derivatives thereof, increase the wrinkle recovery values. However, due to the employment of acid catalysts and the need for high temperatures ($> 120^{\circ}\text{C}$), the cotton physical strength properties such as breaking strength, elongation, tearing strength, abrasion resistance are severely decreased. The base catalyzed process as developed does not involve chemical reaction (cross-linking) with cotton substrate and hence, as expected, the resulting product does not show any appreciable improvement in the wrinkle recovery. The improved physical strength properties of the encapsulated cottons are attributed to the deposition of high molecular weight polyoxymethylene in conjunction with the use of relatively weak basic catalyst which does not attack the cotton substrate.

Thermal stabilization of the polyoxymethylene homopolymer hydroxyl end groups, previously described as "end-capping", has been effected by using acetic anhydride, which is monofunctional. The employment of difunctional anhydrides such as maleic anhydride and/or other multifunctional compounds should render it possible to crosslink the cotton as well as to "end-cap" the polyoxymethylene homopolymers. Such multifunctional compounds should increase the wrinkle recovery values without deteriorating the improved physical strength properties of the polyoxymethylene coated cotton fabrics.



D. Nylon 610

This continuous process describes a novel method of depositing Nylon 610 polymers on sebacoyl chloride impregnated cloth substrates by reacting the sebacoyl chloride with the hexamethylene diamine vapor.

The major problem encountered with this interfacial liquid/vapor phase polymerization system is, of course, the formation of by-product HCl. Unless reaction conditions are suitably arranged, this HCl by-product will and does attack and quickly deteriorate the cotton cloth. Furthermore, the sebacoyl chloride hydrolyzes quite readily in the presence of even small amounts of moisture also resulting in HCl formation. This can be minimized by the use of an anhydrous organic solvent, e.g. carbon tetrachloride or equivalent. Prompt neutralization is indicated in order to render the HCl innocuous.

IV. Summary

The following have been accomplished in this investigation:

(1) Reproducible and effective methods have been developed for the vapor phase encapsulation of cotton fiber cloth samples using monomer vapors such as ethylacrylate, glycidyl methacrylate, formaldehyde, ethylene, and sebacoyl chloride/hexamethylene diamine and employing acidic as well as basic catalyst systems.

(2) Photomicrographic studies reveal that at low polymer add-ons, the polymer coatings are relatively continuous and smooth. However, as the polymer build up increases, clumps or "dendrites" begin to form with increasing frequency and in some cases, the coatings become discontinuous.



Cross sections of cotton fibers show that at the so-called cross-over points, cementation of polymer takes place. The polymer growth mechanism is probably a two step process. The initial growth phase appears to be essentially substrate surface controlled and the polymer deposits are uniform and smooth. As the polymer build up increases, the deposition becomes less surface controlled and increasingly irregular growth takes place.

(3) While encapsulation alone cannot improve all the desirable physical properties of cotton, substantial improvements can be made in selected properties. The data suggest that encapsulation has to be combined with some type of chemical reaction with the fibers (crosslinking) to enhance properties such as wrinkle recovery.

(4) Formaldehyde and sebacoyl chloride/hexamethylene diamine based coatings offer the most promise for upgrading physical properties of cotton. "End-capped" polyoxymethylene coating is particularly attractive; strength properties such as breaking strength and elongation, tearing strength, abrasion resistance, have all been improved considerably. Wrinkle recovery values could be improved by "end-capping" of the hydroxyl end-groups of polyoxymethylene homopolymers with difunctional anhydrides such as maleic anhydride and/or other multifunctional compounds. These compounds should render it possible to cross-link the cotton as well as to "end-cap" the polyoxymethylene homopolymers.



In the sebacoyl chloride/hexamethylene diamine system, the HCl generated in the gaseous interfacial treatment could be utilized for cross-linking reaction using a methylol amide cross-linking agent. This reaction could be carried out in a number of ways including the impregnation of the cotton cloth samples with a methylol amide cross-linking agent followed by drying; followed by application of the dibasic acid chloride (sebacoyl chloride) and exposure to the hexamethylene diamine vapors.



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